

# Accepted Manuscript

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PII: S0045-6535(18)31170-6

DOI: 10.1016/j.chemosphere.2018.06.095

Reference: CHEM 21627

To appear in: *Chemosphere*

Received Date: 08 December 2017

Accepted Date: 12 June 2018

Please cite this article as: Yi-Bo Zhao, Xu-Dong Lv, Hong-Gang Ni, Solvent-based separation and recycling of waste plastics: A review, *Chemosphere* (2018), doi: 10.1016/j.chemosphere.2018.06.095

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1 **Solvent-based separation and recycling of waste plastics: A review**

2 Yi-Bo Zhao <sup>a</sup> Xu-Dong Lv <sup>b</sup> and Hong-Gang Ni<sup>a, \*</sup>

3 <sup>a</sup>Shenzhen Key Laboratory of Circular Economy, Shenzhen Graduate School, Peking  
4 University, Shenzhen 518055, China

5 <sup>b</sup>College of Chemistry and Chemical Engineering, Northwest Normal University,  
6 Lanzhou 730070, China

7

8 **Corresponding Author**

9 Phone: +86-755-26033017. Fax: +86-755-26033254. E-mail: nihg@pkusz.edu.cn

10

**11 Abstract:**

12 Since the creation of first man-made plastic, the global production and consumption of  
13 plastics have been continuously increasing. However, because plastic materials are  
14 durable and very slow to degrade, they become waste with high staying power. The over-  
15 consumption, disposal, and littering of plastics result in pollution, thus causing serious  
16 environmental consequences. To date, only a fraction of waste plastics is reused and  
17 recycled. In fact, recycling plastics remains a great challenge because of technical  
18 challenges and relatively insufficient profits, especially in mixed plastics. This review  
19 focuses on an environmentally friendly and potentially profitable method for plastics  
20 separation and recovery and solvents extraction. It includes the dissolution/reprecipitation  
21 method and supercritical fluid extraction, which produce high-quality recovered plastics  
22 comparable to virgin materials. These methods are summarized and discussed taking  
23 mass-produced plastics (PS, PC, Polyolefins, PET, ABS, and PVC) as examples. To  
24 exploit the method, the quality and efficiency of solvent extraction are elaborated. By  
25 eliminating these technical challenges, the solvent extraction method is becoming more  
26 promising and sustainable for plastic issues and polymer markets.

27 **Keywords:** waste plastics; solvent extraction; dissolution/reprecipitation; supercritical  
28 fluid extraction

## 29 **1. Introduction**

30 The challenge of the disposal of accumulated waste plastics and corresponding  
31 environmental issues have received widespread attention from the public and  
32 academicians (Rochman et al., 2013; Jambeck et al., 2015). Waste plastics can turn into  
33 the resources for new plastic products; thus, a cyclic economy can be achieved by  
34 coupling waste prevention with material recycling. For example, a sequential extraction  
35 process using mixed solvents to recover polycarbonates can obtain a high yield (>95%)  
36 and high purity similar to virgin polycarbonates recycled product using less energy  
37 (Weeden et al., 2015). Although green chemistry has grown remarkably (Cui et al.,  
38 2011), large amounts of waste plastics remain for safe disposal and reutilization.  
39 Recycling plastics can also be viewed as a big business because of its potential  
40 environmental benefits and economic profits. However, about 6300 million metric tons of  
41 plastic waste have been generated until 2015, and only 9% of them are recycled, 12% are  
42 incinerated, and 79% are discarded (Fig. 1) (Geyer et al., 2017). Taking the fastest-  
43 growing component of the municipal solid waste stream as an example, electronic waste  
44 (e-waste, global generation 20–50 million tons/year (Robinson, 2009; Herat and  
45 Agamuthu, 2012)) contains valuable plastics (~30%) (Gramatyka et al., 2007). In fact, e-  
46 waste plastics consist of heterogeneous polymers, which makes the recycling process  
47 difficult (Schlummer et al., 2006; Ignatyev et al., 2014), such as ABS, PC, SAN, PS  
48 (Beigbeder et al., 2013), PP, and PET (Martinho et al., 2012). Nevertheless, recycling the  
49 e-waste plastics with environment-friendly technology necessarily contributes to reducing

50 oil and energy consumptions (Ignatyev et al., 2014), decreasing CO<sub>2</sub> emission (Allwood  
51 et al., 2010), and lowering costs of production (Weeden et al., 2015).  
52  
53 Nowadays, most of waste plastics are landfill (Barba-Gutiérrez et al., 2008) or  
54 incineration, contributing to amounts of toxic pollutants (Li et al., 2001; Schlummer et  
55 al., 2007a). In addition, microplastics resulting from human material and product use or  
56 derived from the breakdown of larger plastic debris are the newest emerging contaminant  
57 in the environment at high levels, particularly in aquatic and marine ecosystems  
58 (Rochman et al., 2013). However, no substantial increase in recycling plastics is observed  
59 yet likely due to the high recovery requirement and costs of disposal (Stein, 1992;  
60 Ignatyev et al., 2014; Perrin et al., 2016). The average global recycling rate is about only  
61 18%, and in particular, the recycling rates in Europe, China, and the United States are  
62 30%, 25%, and 9%, respectively (Geyer et al., 2017). Current methods of plastic recovery  
63 include mechanical recycling, solvent recycling, pyrolysis, and gasification (Hamad et  
64 al., 2013; Wang and Xu, 2014). Among these methods, mechanical recycling and  
65 chemical recycling (e.g., pyrolysis) are the most widely practiced (Hamad et al., 2013).  
66 Recycling of waste plastics by segregating mixed wastes into a homogenous polymer  
67 (e.g., mechanical recycling) leads to a broader application and higher value (Braun, 2002;  
68 Sadat-Shojai and Bakhshandeh, 2011). In terms of life cycle assessment, mechanical  
69 recycling is more attractive with a smaller environmental burden (e.g., consumption of  
70 fewer resources and lower impact on global warming) (Dodbiba et al., 2008).

71 Considering the decision variables such as the economic, environmental, and  
72 technological performance, mechanical recycling is the most suitable for manufacturing  
73 organizations also (Vinodh et al., 2014). Compared with other mechanical recovery  
74 methods (e.g., manual sorting and floatation), plastic recycling by solvent extraction has  
75 been proved to purify recovered plastics efficiently (Vane and Rodriguez, 1992).

76

77 As a secondary mechanical recycling, plastic recycling by solvent extraction is a  
78 promising method with widespread application in waste plastic recovery (Cervantes-  
79 Reyes et al., 2015), and studies on this topic are mounting in recent four decades (Drain  
80 et al., 1983; Vane and Rodriguez, 1992). Unfortunately, to the best of our knowledge, no  
81 primary summary of the solvent extraction of plastic has been provided yet. Many articles  
82 have been published regarding this approach for the separation and recovery of various  
83 waste plastics, and here, we provide a critical review of all the relevant studies. This  
84 review attempted to review the literature on current solvent extraction methods  
85 (dissolution/precipitation technique and supercritical fluid (SCF) extraction (SFE)) of  
86 recycling different types of plastics under specific conditions (e.g., different temperatures  
87 and pressures). The polymer dissolution mechanism was included to better understand  
88 how this method worked. To enhance this method, the solutions to improve the quality  
89 and efficiency of solvent extraction recovery are also discussed.

90

91 **2. Basic information of extraction with solvents**

92 The generic framework of plastic recycling by solvent extraction includes the removal of  
93 impurities (such as SFE, MAE, ASE, and other plastic additives), dissolution  
94 (homogeneous or heterogeneous dissolution), and reprecipitation or devolatilization.  
95 Specifically, the polymer(s) is dissolved in the solvent(s), and then each polymer is  
96 selectively crystallized. Ideally, when a solvent can dissolve either the target polymer or  
97 all the other polymers except the target one, it can be used to for selective dissolution.  
98 Obviously, the key to dissolution process is finding a selective solvent.

99

#### 100 *2.1. Experimentally observed dissolution phenomena*

101 The dissolution process is affected by the types of polymers and solvents (Achilias et al.,  
102 2007; Hadi et al., 2014), polymer size, molecular weight of polymer (Gutierrez et al.,  
103 2013a), dissolution temperature (Achilias et al., 2009a; Gutierrez et al., 2013a; Hadi et  
104 al., 2014), dissolution time (Achilias et al., 2009a; Gutierrez et al., 2013a; Hadi et al.,  
105 2014), and concentration (Achilias et al., 2009a). Thermodynamically, two transport  
106 processes are involved during polymer dissolution, solvent diffusion and chain  
107 disentanglement (Miller-Chou and Koenig, 2003b). During chain disentanglement, the  
108 self-diffusion of the polymer plays the important role (Martini et al., 2006). With the  
109 increase in the polymer molecular weight, the dissolution becomes disentanglement  
110 controlled instead of diffusion controlled (Narasimhan and Peppas, 1996). In general, a  
111 gel-like swollen layer appears with two separate interfaces because of the plasticization  
112 of polymer during dissolution. That is, separate interfaces form between the glassy

113 polymer and the gel layer and between the gel layer and the solvent. According to the  
114 surface lay formation process outlined by Ueberreiter (Ueberreiter, 1968), the solvents  
115 push the swollen polymer into the solvent, and further infiltration of the solvent into the  
116 polymer increases the swollen surface layer until a quasi-stability state is reached.  
117 Kinetically, solvent dissolution depends on the solvent size and the free volume of the gel  
118 phase (Devotta and Mashelkar, 1996). The dissolution times decrease with the decrease  
119 in particle size and increase in the diffusivity of polymers, because of the increased mass  
120 transfer rate (Miller-Chou and Koenig, 2003b). For example, the dissolution rates of  
121 PMMA increased with the addition of small-molecule nonsolvent (Cooper et al., 1986).  
122 In fact, the polymer dissolution mechanisms are very complicated. Therefore, only  
123 dissolution phenomena are summarized in qualitative terms here. More details of polymer  
124 dissolution mechanism can be found in a previous review (Miller-Chou and Koenig,  
125 2003b).

126

127 The structure of glassy polymers has an infiltration layer, a solid swollen layer, a gel  
128 layer, and a liquid layer (Fig. 2). In the glassy state, the polymer contains channels and  
129 holes of molecular dimensions. The solvent molecules fill these empty spaces and start  
130 the diffusion process without creating new holes. All layers are formed in “normal  
131 dissolution,” whereas the gel layer disappears as a consequence of the decrease in stress  
132 energy; this indicates the transition from normal dissolution to cracking. The insoluble  
133 polymers are assumed as the additional layer by decreasing the diffusion of both solvents

134 and polymers (Martini et al., 2009). Typically, normal dissolution involves the  
135 penetration of the solvent, swelling of the polymers, and diffusion into the solvent  
136 (Stamatialis et al., 2002).

137

138 In reality, many factors affect polymer dissolution, such as molecular weight,  
139 composition, and structure of the polymer and composition and size of the solvent  
140 (Miller-Chou and Koenig, 2003a). As an example, cracks in PMMA and PS occur earlier  
141 with benzene than with toluene, because of the higher vapor pressure and smaller size of  
142 benzene (Miller-Chou and Koenig, 2003a). Consequently, benzene dissolves PMMA and  
143 PS faster than toluene. In terms of the composition of the solvent, the presence of a small  
144 portion of nonsolvent in the solvent mixture can improve the dissolution of polymers  
145 (Miller-Chou and Koenig, 2003a). Furthermore, the addition of low-molecular weight  
146 nonsolvent in certain ranges also results in the reduction in swelling (Devotta and  
147 Mashelkar, 1996). Apparently, this indicates a more quantitative design of mixed  
148 solvents. Under supercritical conditions, the high pressure of SCFs results in the swelling  
149 of polymers, which can be decreased by heating (Kazarian and Chan, 2004). Therefore, a  
150 balance between the pressure and temperature should necessarily be achieved.

151

## 152 *2.2. Solvent selection*

153 The common solvents employed in the dissolution/reprecipitation method are shown in  
154 Table 1. Solvents and nonsolvents for polymers used in the dissolution/reprecipitation

155 method were primarily summarized by Fuchs and Suhr (Fuchs and Suhr, 1989). The  
156 optimal solvents are primarily selected by following several major principles (Jilin,  
157 2010). (1) According to the solubility rule “like dissolves like,” high polar polymers are  
158 dissolved in high polar solvents, while low polar polymers are dissolved in low polar  
159 solvents. The closer the solvent and polymer are in polarity, the easier it is to dissolve the  
160 polymer in the solvent; (2) when the interaction (detailed below) between the polymer  
161 and solvent prevails over the cohesion of the polymers, the polymer is easily dissolved in  
162 the solvent; (3) if the solubility parameters of the polymer (e.g.,  $\delta_D$ ,  $\delta_P$ ,  $\delta_H$ ) and solvent are  
163 similar or equal, the polymer is more readily dissolved in the solvent. Several solubility  
164 parameter systems are developed to evaluate the solvation ability, such as Hansen  
165 (Hansen and Just, 2001), Kamlet-Taft (Taft et al., 1985), Gutmann (Gutmann, 1976),  
166 Swain (Swain et al., 1983), and  $E_T(30)$  systems (Weerachanchai et al., 2014). The  
167 solubility parameter systems should be selected properly for specific recycling. For  
168 instance, the combination of Gutmann and Kamlet-Taft parameters is the best option for  
169 separating PVC from PET fibers (Grause et al., 2017).

170

171 Suitable solvents are selected by the prediction of HSP values, which is one of the  
172 solubility parameters. The HSP values account for three types of interaction:  $\delta_D$ ,  $\delta_P$ , and  
173  $\delta_H$  (Fig. 3). The HSP values are temperature dependent and also affected by the molecular  
174 size and molecular shape (Hansen, 2002). The solubility parameter “distance”  $R_a$  between  
175 a polymer (subscript 1) and the solvent (subscript 2) is defined as follows:

$$176 \quad (R_a)^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \quad (1)$$

177 The relative energy difference (RED) is defined as the ratio of  $R_a$  to  $R_0$ :

$$178 \quad \text{RED} = R_a / R_0 \quad (2)$$

179 where  $R_0$  is the radius of sphere and  $R_a$  is the distance from a given solvent point to the  
180 center of the sphere. RED value indicates the extent of polymer solubility in a solvent:

- 181 ● RED < 1, soluble and high affinity; strong solvent
- 182 ● RED > 1, nonsoluble and low affinity; weak solvent
- 183 ● RED ≈ 1, partially soluble; boundary condition

184 In addition, solvents cracking the polymers have RED values in the range 0.8 to 1.0,  
185 while solvents dissolving the polymers have RED values of less than 0.8 (Hansen and  
186 Just, 2001). According to a previous study (Weeden et al., 2015) (Table 1), the  
187 predictions of HSP were confirmed except for isopropyl alcohol and THF. Sometimes the  
188 real situations challenge the HSP theory, because this theory overlooks electrostatic  
189 forces (Weeden et al., 2015) and the interactions between the solvent and polymers. For  
190 instance, some solvents with RED < 1 still cannot dissolve the polymer. Accordingly, the  
191 solubility result based on the HSP theory has to be confirmed by a solubility test  
192 experiment.

193

194 Several factors should be considered during the practical application, such as the  
195 dissolution ability of the solvent, viscosity, toxicity, time consumed for the dissolution,  
196 forms of the obtained polymer, and cost (Sperber and Rosen, 1976; Pappa et al., 2001). In

197 a very recent study (Zhao et al., 2017), these factors were considered in the separation  
198 and recycling of PS, PC, ABS, and SAN. In particular, suitable solvents have to be used  
199 to leave one polymer in solid state in each step. It is also noted that the selected solvents  
200 may vary depending on the plastic compositions. Toxic solvents even with ideal  
201 dissolution ability were not recommended to establish the recycling method. A moderate  
202 viscosity is required to facilitate stirring and centrifugation. Recycling methods with a  
203 long processing time were not practical for industrialization. The recycling method for  
204 PC- and PS-dominated plastics was money and energy saving. Besides, the forms of  
205 recovered polymers such as grains and fibers were applicable for reuse (Pappa et al.,  
206 2001).

207

208 Under supercritical conditions, density is also one of the factors that determine the  
209 solvent strength and solubility, besides high pressure and high temperature (Martini et al.,  
210 2006). The relationship between the solubility of the solutes and the density of the  
211 solvents is as follows (Chrastil, 1982):

$$212 \quad C = \rho^k \exp[(a/T) + b] \quad (3)$$

213 where  $C$ (g/L) is the concentration of a solute in the solvent (usually less than 100-200  
214 g/L);  $\rho$  (g/L) is the density of SCFs;  $k$  is the association number of the solute; and  $a$  and  $b$   
215 are the variables related to the solvent and the solute, respectively. The solubility of the  
216 solute is closely related to the SCFs' density than to its pressure (Chrastil, 1982). In  
217 particular, the solubility of solute increases with either higher density or higher

218 temperature of SCFs (Martini et al., 2006). Compared with energy-consuming  
219 technologies such as pyrolysis, SFE has a potential of less environmental impact but a  
220 high energy consumption (Wang and Xu, 2014).

221

### 222 *2.3. Summary of plastic recycling through solvent extraction*

223 The kernel of this methodology is the selective dissolution process using traditional  
224 solvents or an SCF. For the dissolution/precipitation technique, there are two categories  
225 of solvents: “strong solvent,” which has a positive solubility to the target polymer and  
226 “weak solvent,” which has a negative solubility to the target polymer. Fig. 4 and Table 2  
227 describes the dissolution/precipitation method (Poulakis and Papaspyrides, 1997). The  
228 advantages of the dissolution/precipitation method are also summarized in Table 2  
229 (Kampouris et al., 1988; Poulakis and Papaspyrides, 1997; Poulakis et al., 1997).

230

231 SFE is a relatively new recycling process for extracting polymers from waste, including  
232 supercritical antisolvent precipitation (Yeo and Kiran, 2005). SCFs possess intermediate  
233 properties between liquids and gases (Ajzenberg et al., 2000). Theoretically, SFE offers  
234 many advantages compared with classical solvents method, such as the improvement in  
235 mass transfer, better extraction time and efficiency, minimal residues in the final product,  
236 and no residues of organic waste (Ben Said et al., 2016). To date, SCFs have commonly  
237 been used in selective depolymerization (chemical recovery). However, their use in  
238 physical recovery is increasing rapidly in recent years. SCFs possess similar solubility

239 and transport properties as those of organic solvents and gases, respectively. Particularly,  
240 carbon dioxide is the most widely used SCF because it is nonpoisonous, nonpolluting,  
241 and of low cost (Peng et al., 2014). The polymers are dissolved in solvents and then  
242 extracted by SCFs subsequently (Fig. 5).

243

244 Non-green solvents (e.g., some organic solvents) are not environmentally friendly and  
245 may limit the applications of recovered polymers (e.g., food packaging) (García et al.,  
246 2009a). Green solvents are of high costs and environmentally friendly. For instance, SFE  
247 may be often more costly than the conventional method (Knez et al., 2014). With regard  
248 to costs, equipment, energy consumption, and solvent losses in conventional solvent  
249 dissolution/re-precipitation method are discussed (Zhao et al., 2017).

250

### 251 **3. Exemplary cases of polymer recovery**

#### 252 *3.1 Homogeneous fractionation*

##### 253 *3.1.1 PS*

254 Because of the high formability and resistance to acids and alkalis, PS is widely used in  
255 packaging and electronic products. However, its nondegradability and low density lead to  
256 serious white pollutions. The large volume of PS results in transportation problems and  
257 higher costs.

258

259 PS can be dissolved in both environmentally benign (Noguchi et al., 1998a; Noguchi et

260 al., 1998b; García et al., 2009a; Hearon et al., 2014; Gutiérrez et al., 2015) and toxic  
261 solvents (Achilias et al., 2009a; Yang and Yang, 2012). Limonene, terpinene, cymene,  
262 and phellandrene were investigated as the best solvents for recycling XPS (García et al.,  
263 2009a). Similarly, limonene acts as be a good solvent and antioxidant for EPS even  
264 during the heating process (Noguchi et al., 1998b). A previous study found that D-  
265 limonene as a diene monomer in thiol-ene reactions dissolves PS for PS reclamation from  
266 solution (Hearon et al., 2014).

267

268 MEK/methanol, MEK/n-hexane, and p-xylene/n-heptane proved to be satisfactory  
269 systems for recycling PS foam (Kampouris et al., 1987). The dissolution/reprecipitation  
270 method can also be used to recycle polymers from packaging waste in a  
271 solvent/nonsolvent system (Achilias et al., 2009b). Conventional solvents (e.g.,  
272 xylene/methanol) are applied to recycle the model PS at different dissolution  
273 temperatures. In a certain temperature range, a high temperature contributed to a high  
274 recovery of the PS. Considering the environmental impact, a more environment-friendly  
275 solvent (D-limonene, extracted from the rinds of citrus fruits) was used to recover 100%  
276 EPS (Noguchi et al., 1998a; Noguchi et al., 1998b). Despite possible chain thermal  
277 degradation caused by a slight decrease in the average molecular weight, the chemical  
278 structure of the polymer was not significantly altered.

279

280 The solvent removal may present disadvantages during solvent recovery. For example,

281 the formation of byproducts from the thermal degradation of polymer chains during  
282 solvent removal and the residues of “good solvents” such as aromatic compounds limit  
283 further applications (Gutierrez et al., 2012). Nevertheless, SCFs could overcome this  
284 disadvantage by removing the solvent completely. Therefore, SCFs have been widely  
285 applied to separate polymeric matrices and solvents, especially SCCO<sub>2</sub> (Ben Said et al.,  
286 2016). Supercritical CO<sub>2</sub> is a slightly polar solvent and cannot dissolve strong polarity or  
287 hydrogen-bonded polymers (Rindfleisch et al., 1996). CO<sub>2</sub> is a poor solvent for high-  
288 molecular weight polymers under specific conditions (Gutierrez et al., 2012). The studies  
289 showed that CO<sub>2</sub> dissolved the PS of molecular weight less than 1000 (Rindfleisch et al.,  
290 1996), and PS of high molecular weight (1700 g/mol) was insoluble under the condition  
291 of 3000 psia at 35 °C (O'Neill et al., 1998). Therefore, it is a practical recovery method  
292 for high-molecular weight PS in commercial products. Gutierrez et al. proposed an  
293 environmentally friendly method for recycling PS (Gutierrez et al., 2016). The process  
294 consists of the dissolution of PS in limonene and the removal of solvents using  
295 supercritical CO<sub>2</sub>. The optimum conditions were a high pressure ( $\geq 100$  bar), low  
296 temperature ( $\leq 30^\circ\text{C}$ ), and moderate concentration ( $\leq 0.4$  g PS/mL limonene). In another  
297 related literature, CO<sub>2</sub> acts as the antisolvent for the precipitation of PS in p-Cymene  
298 (Gutiérrez et al., 2014).

299

### 300 3.1.2 PC

301 PC is one of the most widely used engineering thermoplastics because of its excellent

302 physical and chemical properties. To date, considerable research has been conducted to  
303 treat this kind of waste polymer. By using the dissolved/reprecipitation method, Achilias  
304 et al.(2009a) focused on the recycling of three types of polymers from e-waste, namely  
305 PC, ABS, and PS. They recovered these model polymers using three pairs of  
306 solvent/nonsolvent systems, namely dichloromethane (DCM)/methanol,  
307 acetone/methanol, and chloroform/methanol, respectively. The recovery of PC reached  
308 98% even at a low temperature using the DCM/methanol system. For the same solvent  
309 pair, the result of e-waste plastic recycling was identical to that of the model polymer. No  
310 significant difference was found in the chemical structure between the two recycled  
311 polymers; this indicates that no thermodynamic degradation occurred during the  
312 dissolved/reprecipitation process.

313

### 314 *3.1.3 Polyolefins (LDPE, HDPE, and PP)*

315 LDPE and HDPE, the major types of thermoplastics, are widely used in the manufacture  
316 of bags, toys, containers, pipes, house-wares, and industrial wrappings (Achilias et al.,  
317 2007). Poulakis and Papaspyrides (1995) proved toluene/acetone as a potential  
318 solvent/nonsolvent for recycling PE. The recyclates exhibited a strong retention of melt  
319 flow index, molecular weight, crystallinity, mechanical performance, and grain size.  
320 Achilias et al. (2007) investigated toluene/n-hexane and xylene/n-hexane (v:v=1:3) as a  
321 solvent system for recycling polyolefins by the dissolution/reprecipitation method and the  
322 effects of solvent types and dissolution temperature on recovery values. They found no

323 significant structure difference between the model and recycled polymers. At the same  
324 time, they also observed that the tensile strength at maximum load levels of the recycled  
325 product could be comparable to that of virgin polymers. However, the elastic modulus  
326 increased because of the fractionation phenomenon that occurred during the recycling  
327 process. Similarly, xylene and toluene were used as solvents, while n-hexane as  
328 nonsolvent in a volume ratio of 1:3 (solvent:nonsolvent) in the study by Achilias et al.  
329 (2008).

330

331 On the basis of the dissolution/re-precipitation method, a new, low-cost, pure or blend  
332 solvent system to recycle polyolefin was developed by Hadi et al. (Hadi et al., 2013). In  
333 their study, pure turpentine, turpentine/PetE, and turpentine/benzene as solvents with  
334 different fractions and PetE and n-hexane as weak solvents were examined. To reduce  
335 cost and obtain the recycled polymer in the form of powder or granules, the effects of  
336 sample concentration, dissolution temperature, dissolution time, and type of waste plastic  
337 products were determined. In terms of chemical structure, the thermal and tensile  
338 mechanical properties of the recycled polymer did differ from those of virgin polymer.  
339 Further work on this dissolution/re-precipitation method with different solvents (xylene,  
340 n-hexane, and petroleum ether grades A, B, and C with boiling points of 40-60 °C, 60-80  
341 °C, and 90-120 °C, respectively) for recycling LDPE, HDPE, and PP also suggested that a  
342 high temperature and a low polymer concentration lead to a high polymer recovery in a  
343 limited range (Hadi et al., 2014).

344

345 PP works individually or with ethylene as a copolymer and is widely used in the  
346 manufacture of ropes, plastic bottles, and electric products. Recycling PP with solvent  
347 techniques has been studied for years (Murphy et al., 1979). Various solvent systems  
348 were examined. Murphy et al. (1979) explored tetrachloroethylene/acetone (3:2 in  
349 volume) at 130 °C for recycling PP and at 60 °C-70 °C for drying the recycled product.  
350 Xylene/acetone (1:3 in volume) was used to conduct a model experiment on virgin  
351 material for the recycling of PP (Poulakis and Papaspyrides, 1997). Furthermore, a  
352 different ratio of xylene/acetone (1:7 in volume) was also used to extract PP (Poulakis et  
353 al., 1997).

354

#### 355 *3.1.4 PET*

356 The applications of PET include packaging, overhead-projector films, textiles, and  
357 aluminum-coated reflective materials. Several studies on model PET recycling using  
358 NMP have been published, with the aim of recycling PET bottles. A selective dissolution  
359 process was used to purify recovered PET (Vane and Rodriguez, 1992). NMP/n-octane +  
360 n-hexane was used as a particularly suitable solvent/nonsolvent system in the  
361 dissolution/precipitation method for recycling PET (Poulakis and Papaspyrides, 2001).  
362 The slight decrease in the number-average molecular weight after consecutive recycling  
363 cycles may be related to processing and additives.

364

### 365 3.1.5 ABS

366 ABS is an engineering thermoplastic that involves amorphous-continuous phase  
367 (poly(styreneco-acrylonitrile) copolymer) and rubbery-dispersed phase (dispersed  
368 butadiene or butadiene copolymer). It is mainly used in automotive and electronic casing.  
369 Arostegui et al. (2006) proposed a dissolution-based method with acetone (0.25 g/mL) at  
370 room temperature. FTIR, DSC, and MFI indicated that the solvent-based method does not  
371 degrade ABS. However, the dissolution and injection molding may accelerate the  
372 degradation by the elimination of stabilizers, reduction in molecular weight, and  
373 butadiene degradation.

374

### 375 3.1.6 PVC

376 PVC is one of the most widely consumed thermoplastic materials (Sadat-Shojai and  
377 Bakhshandeh, 2011). Particularly, it is also present in electronic and electrical equipment.  
378 This kind of plastic, along with toxic additives and BFRs, hinders the recycling into  
379 higher grade products (Tansel, 2017). Accordingly, PVC is necessarily extracted from  
380 waste stream. Besides, it was claimed that the profile properties of PVC recyclate for new  
381 applications were comparable to those of virgin PVC (Sadat-Shojai and Bakhshandeh,  
382 2011).

383

## 384 3.2 Homogeneous fractionation

### 385 3.2.1 Dissolution/reprecipitation technique

386 More recently, Weeden et al. developed a room-temperature sequential extraction using  
387 DCM/ACE (v:v=1:1) to recycle PC from e-waste (recovery>95%); the results showed  
388 that the method was 30% cheaper and used 84% less energy compared with those in the  
389 production of virgin PC from petroleum (Weeden et al., 2015). Pappa et al. (2001)  
390 studied the separation of LDPE, HDPE, and PP by xylene/propanol-1 (1:3 in volume) in a  
391 pilot unit and found that it could achieve economic profits with a large scale of 30000  
392 t/year. According to their study, the recovery can be profitable compared with the use of  
393 virgin polymers. A solubility-based technique known as CreaSolv<sup>®</sup> process (a potential  
394 commercial solvent-based recovery technique in Europe) was employed to separate HIPS  
395 and ABS by removing contaminants such as flame retardants (Schlummer et al., 2006;  
396 Nnorom and Osibanjo, 2008). More recently, researchers investigated the separation of  
397 PC and ABS using CreaSolv<sup>®</sup> process at a laboratory scale (Schlummer et al., 2016). In a  
398 concrete example of separating blended textiles, 96% PET was recovered by ACE or  
399 N,N-dimethylformamide through Soxhlet extraction (Sun et al., 2013). More recently,  
400 Zhao et al. proposed a procedure for separating and recycling PC, PS, ABS, and SAN,  
401 with DCM, ACE, and ACN. The recovered polymers were yielded with high purities and  
402 without degradation (Zhao et al., 2017).

403

404 In practice, PVC can be separated from PS by cyclohexanone/hexane (solvent/nonsolvent  
405 system) (Kampouris et al., 1986). A mixture of xylene/cyclohexanone (85:15 in volume)  
406 could convert the PVC into a solution (Sperber and Rosen, 1976). Several operated

407 projects such as Vinyloop® have been developed by the dissolution/reprecipitation  
408 technique in the close loop (Sadat-Shojai and Bakhshandeh, 2011). However, details  
409 about the resources, particularly the solvents of those operated projects, are unknown  
410 (Tukker, 2002). For waste PVC pipes, Qiao et al. (2007) used organic solvents to separate  
411 PVC with a recovery rate of 86% at room temperature in 24 h from inorganic substances  
412 (CaCO<sub>3</sub>). In another study, THF, cyclohexanone, and cyclopentanone were efficient in  
413 dissolving PVC from PET fibers (Grause et al., 2017).

414

### 415 *3.2.2 Supercritical fluid extraction*

416 By near-critical selective solubilization, PP can be dissolved by n-pentane and n-heptane  
417 at supercritical pressures and above the polymer melt temperature from PP/PS blends  
418 (Martini et al., 2006).

419

### 420 *3.3 Implications for future applications*

421 The investigations mentioned above claimed that the mechanical properties of the  
422 recycled products were comparable with those of virgin plastics by using the solvent  
423 extraction method. Therefore, this method is proved to be an efficient way to separate and  
424 recycle plastics. According to previous studies (Weeden et al., 2015; Zhao et al., 2017),  
425 the method harbors definite environmentally friendly properties, compared with the  
426 virgin polymers produced from oil products. Economically, the recovery processes  
427 performed differently. For example, the cost of recycling PC from e-waste was 30%

428 lower than that for the production of virgin polymers (Weeden et al., 2015). In contrast,  
429 the plastic composition greatly affects the recovery cost (Zhao et al., 2017). The recycling  
430 processes should be feasible only if plenty of wastes were treated (Gutierrez et al., 2016).

431

#### 432 **4. Quality and efficiency of solvent extraction recovery**

433 For quality assessment of recovered plastics, three quality aspects must be considered.  
434 Namely, the composition pattern, the physicochemical property degradation (chemical  
435 and morphological changes and mechanical and rheological property changes; Fig. 6),  
436 and the presence of low-molecular weight impurities (solvent residues, additives, and  
437 degradation products) (Karlsson, 2004; Stangenberg et al., 2004). Hence, strategies of  
438 producing high-quality materials from waste plastics, such as re-stabilization, rebuilding,  
439 compatibilization, and addition of elastomers and fillers, are often applied to assure  
440 performance in new applications (Vilaplana and Karlsson, 2008).

441

##### 442 *4.1. Polymer identification and property testing*

443 To determine the additives and choose suitable solvent pairs for recycling, the  
444 composition of waste polymer should be analyzed first. Table 3 lists a variety of  
445 assessment techniques for recovering polymers. FTIR is used to identify different  
446 polymers in waste plastics by comparing the spectra of the waste sample with that of  
447 model polymers (Achilias et al., 2009b). Unlike FTIR and DSC, NIR and Raman  
448 spectroscopy can perform fast and reliable compositional analysis without sample

449 pretreatment (Camacho and Karlsson, 2001; Vilaplana and Karlsson, 2008). They can  
450 also examine potential structure changes of recovered products. HPLC is used to analyze  
451 mixed polymers. After the dissolution process, a small amount of low-molecular weight  
452 polymer was lost in the extraction steps (Weeden et al., 2015). There are two ways to  
453 determine the molecular weight distribution of the recycled polymer: viscosity method  
454 and GPC. Thermal properties (e.g., melting point, crystallinity, and thermal history) and  
455 the characterization of polymer compositions (before and after recycling) are often  
456 determined with thermal analysis techniques, particularly DSC. DSC is readily employed  
457 for the analysis of polymers of above 1% wt. composition fraction (Camacho and  
458 Karlsson, 2001). As one of the thermal analysis techniques, TGA can be used to examine  
459 the thermal decomposition and to analyze the recovered polymers in terms of humidity,  
460 volatiles, additives, fillers, and nonpolymeric contaminants (e.g., metal particles)  
461 (Vilaplana et al., 2007; Vilaplana and Karlsson, 2008). Long-term thermal and thermo-  
462 oxidative stability of recycled polymers including oxidation temperature and oxidative  
463 induction time can be assessed by DSC, TGA, and CL techniques (Camacho and  
464 Karlsson, 2002).

465

#### 466 *4.2. Additives and impurities*

467 Plastic materials absorb and contain low-molecular weight compounds and potential  
468 contaminants (Camacho and Karlsson, 2000), such as BFRs, stabilizers, and impact  
469 modifiers. During the service life, both the polymer itself and additives undergo

470 multispeed degradation (Moeller et al., 2008). Considering the potential effects on the  
471 properties of recovered polymers, additives must be separated from waste plastics before  
472 recovery. The presence of additives such as BFRs results in large amounts of plastic  
473 disposal through landfills (Paine et al., 2014). Additionally, other polymer residuals in  
474 recovered polymers may also limit the feasibility of recovery (Balart et al., 2005).

475

476 Several methods have been developed for the extraction and determination of polymer  
477 additives (Vandenburg et al., 1997). They are summarized in Table 4. Apparently,  
478 compared with the conventional Soxhlet extraction, those new extraction methods are  
479 more efficient, fast, and consumes less solvent (Ranz et al., 2008). For instance, BFRs  
480 from plastics are easily extracted with SCFs (Wang and Xu, 2014), solvothermal  
481 treatment (Zhang and Zhang, 2012), ionic liquids (Lateef et al., 2008), and MAE (Ranz et  
482 al., 2008). Additionally, MAE coupled with GCMS (Li et al., 2009) and HPLC–UV  
483 (Vilaplana et al., 2009) can successfully extract and quantify BFRs by hexane/water and  
484 isopropanol/n-hexane, respectively. Vilaplana et al. (2008) provided a comparative  
485 analysis of various extraction methods including PLE, MAE, and UAE under different  
486 conditions. It was found that methanol was the optimal solvent for TBBPA removal from  
487 e-waste plastic in the liquid to solid ratio of 15:1 (mL/g), at 90 °C for 2 h (Zhang and  
488 Zhang, 2012). The available solvent-based options such as Creasolv (for BFR removal)  
489 and Centrevap are potentially commercialized, and Creasolv process is feasible at a scale  
490 of 10000 tons/year (Schlummer et al., 2006; Nnorom and Osibanjo, 2008).

491

492 SFE as a useful tool for additive extraction from polymeric materials was also studied.

493 Arias et al. (2009) developed the SCCO<sub>2</sub> extraction at 45 MPa and 80 °C to extract

494 antioxidant additives (Irganox 1076 and Irgafos 168) from LDPE and HDPE. Anouar et

495 al. (2015) studied the removal of low-molecular weight additives in food grade

496 polyolefin, which acts as contaminants in food packaging materials. Compared with the

497 classic solvent technique, SCCO<sub>2</sub> extraction method was more successful in terms of

498 simplicity, efficiency, and speed. Ben Said et al. (2016) used SCCO<sub>2</sub> (200 bar, 90 °C and

499 7.5 h) to extract artificial contaminants from PP and found that pressure was the most

500 significant positive factor to extraction.

501

502 It is vital to decolorize colored plastics for further applications because the color

503 pigments are serious pollutants for the environment. Low-molecular-weight organic dyes

504 can be removed by the precipitation of the polymers with a nonsolvent, for their higher

505 entropies of solution (Sperber and Rosen, 1976). An investigation was made to recycle

506 pigments by an efficient combination of selective dissolution and evaporation from PVB

507 film (Wang et al., 2012). Titanium dioxide, chromium(III) oxide, and iron(III) oxide in

508 ABS can be removed using acetone/water and CreaSolv<sup>®</sup> SB/CreaSolv<sup>®</sup> SBF (a

509 proprietary solvent formulation) by filtration and centrifugation (Arends et al., 2012). In

510 fact, the recycling processes may lead to color changes (Tiganis et al., 2002; Arostegui et

511 al., 2006). Therefore, we speculate that the physicochemical properties of the coloring

512 matter also changed, thus making the removal of the colored matter difficult.

513

#### 514 *4.3. Compatibility issues of polymers blends*

515 Significant effects of the recycling route on the morphology of the plastics blends indeed  
516 exist and thus affect the mechanical properties of the blends with different compositions  
517 (de Souza et al., 2016). For instance, ABS/HIPS blends obtained by different processing  
518 routes display different elongation at break and impact strength (de Souza et al., 2016).  
519 Nevertheless, because of the relatively high purity (Makenji and Savage, 2012), “self  
520 compatibilization” behavior may support ABS/HIPS blends (20:80 in weight) with  
521 improved performance including mechanical properties (Vazquez and Barbosa, 2017).  
522 This implies that the reuse of polymers requires no rigid purity of recovery. In fact, the  
523 blending of polymers combines the mechanical and physical properties of the  
524 components (Haba and Narkis, 2004). According to their exact use, the purity of the  
525 recovered plastics should have different expectations or requirements. Doing so, we not  
526 only improve the efficiency but also reduce the costs of the solvent extraction method. In  
527 practice, the blends of recycle such as PVC/ABS with poor compatibility and  
528 mechanical properties can still be recommended at an industrial scale (e.g., electrical  
529 housing and interior truck panels) because of low cost (Garcia et al., 2007). Similarly,  
530 PVC/PS are not miscible because of repulsive interactions, and the miscibility can be  
531 improved by using a third polymer (Melad and Mark, 2005). To improve the  
532 characteristics of recycled blended plastics, compatibilizers would be helpful (Vazquez

533 and Barbosa, 2016).

534

#### 535 *4.4. Effect of consecutive recycling cycles*

536 Generally, a slight degradation after the multiple recycles was not manifested in the

537 physical properties of products (Murphy et al., 1979). Poulakis and Papaspyrides (1997)

538 focused on the effect of sample history on mechanical properties through consecutive

539 recycling cycles and indicated no significant differences between the mechanical

540 properties (e.g., yield strength and elongation at break) of virgin and recovered materials.

541 For ABS, no changes were observed for low-strain properties (Young's modulus), but

542 high-strain properties (yield stress and impact strength) decreased during the first

543 recovery of ABS because of butadiene degradation and SAN's lower molecular weight

544 (Arostegui et al., 2006). However, these high-strain properties remained constant in

545 subsequent recycling cycles. Similarly, the MFI and the elongation at break of PP

546 significantly increased from the fifth cycle because of the depletion of stabilizers in

547 previous recycling processes (Aurrekoetxea et al., 2001). Interestingly, even after up to

548 nine cycles, PS still maintained the properties (e.g., mechanical) and stability (Maharana

549 et al., 2007). However, for various polymers, both physical (e.g., the elongation at break)

550 and chemical changes (e.g., chain scission, cross-linking) during the recycling process

551 should be paid special attention to help in ensuring that the recovered polymers are used

552 appropriately (Boldizar and Moller, 2003).

553

554 Molecular weight (MW) distributions of the recovered products were subject to the  
555 recycling processes by the dissolution/reprecipitation method. Some low-MW polymers  
556 may be extracted by solvents after each time of recycling. The MW distribution may play  
557 a crucial role in the mechanical properties of some plastics (Poulakis and Papaspyrides,  
558 1997). For PC, high-MW polymers provide toughness and resistance to environmental  
559 stress cracking, while low-MW polymers can be easily processed (Weeden et al., 2015).  
560 Poulakis and Papaspyrides (2001) found that the MW distribution of PET displayed no  
561 significant difference despite the number of recycling cycles.

562

#### 563 *4.5. Acceptable form of the recycled plastics*

564 Different polymers in various solvents have various forms, such as agglomerates,  
565 powder, granules, and jelly polymer lumps (Papaspyrides et al., 1994). For example, the  
566 gel formation may be caused by the aggregation of particular polymer, which hinders the  
567 separation of solvents and solid products. Fortunately, suitable mix solvents could alter  
568 the precipitation form. Besides, the low-temperature drying results in appropriate forms  
569 of polymers for reprocessing (Drain et al., 1983). Acceptable forms of the recycled  
570 product can be obtained by choosing suitable solvent/nonsolvent pairs (Papaspyrides et  
571 al., 1994). In general, the more acceptable forms include powder and granules instead of  
572 films, sheets, or specific articles (Murphy et al., 1979).

573

574 On the basis of the generic frameworks mentioned above, usually via varied experimental

575 conditions to obtain accepted forms of the recycled product in practice. For example,  
576 Poulakis and Papaspyrides (1997) dissolved PP in xylene at 135 °C that precipitated in  
577 the form of small grains and gained excellent recoveries of both polymer (100%) and  
578 solvents (>90%) without degradation. Smaller particles had higher tensile and impact  
579 strength (de Souza et al., 2016). Another interesting study was conducted by Poulakis and  
580 Papaspyrides (2001) by the grain-size analysis; they found that the grain size of over  
581 94% recycled polymer mass was smaller than 1 mm, which was suitable for further PET  
582 processing.

583

## 584 **5. Conclusion and outlook**

585 Despite the environmentally friendly properties including energy saving and less CO<sub>2</sub>  
586 emission of the current solvent extraction of waste plastics technique (Weeden et al.,  
587 2015; Zhao et al., 2017), it still faces difficulties and challenges, which hinder its  
588 development to some extent. Generally, waste plastics are mixed polymers. Therefore,  
589 the primary challenge is the separation and recycling of waste components one by one  
590 (Hopewell et al., 2009). It is not difficult to understand why those foregoing research  
591 mainly focused on the recycling of single plastic and rarely discussed the disposal of  
592 mixed plastics waste. On the one hand, the dissolution of mixed plastics in solvents (pure  
593 or mixed) is complex and differ from that of individual plastic, because of the  
594 interactions between the solutes. On the other hand, inappropriate formations such as gel  
595 from sequential extraction always hinder the further separation due to difficulties in

596 centrifugation or filtration. More recently, investigations on separation and recovery of  
597 multiple plastics have emerged (Hadi et al., 2012; Zhao et al., 2017).

598

599 Existence of solvents and impurities in the recovered products results in the degeneration  
600 of material properties compared with those of virgin materials. Further, atmospheric or  
601 vacuum distillation also leads to the thermal degradation of polymer chains and worse  
602 plastic quality (Garcia et al., 2009); therefore, the development of proper solvent removal  
603 and purifying techniques (e.g., SFE) is very crucial (Gutierrez et al., 2013b). In reality,  
604 the final products do not have uniform properties due to the inconsistent composition of  
605 solid waste. The presence of a low level of minor polymers is inherent in recycling  
606 scheme (Sperber and Rosen, 1974). Considering both these factors, the balance between  
607 the purity and efficiency in recovery process should also be carefully investigated.

608

609 The life cycle analysis of polymeric materials primarily involves processing, service life,  
610 and further disposal. Specifically, degradation during their service life mostly affects  
611 their recycling and performance in second market (Vilaplana et al., 2006). Obviously, the  
612 appropriate applications were subject to the properties of recycled and upgraded  
613 polymers compared with those of virgin materials (Espert et al., 2004). Environmentally,  
614 the removal of toxic flame retardants (e.g., BFRs) should be conducted at the first step of  
615 recovery (Schlummer and Maurer, 2006; Schlummer et al., 2007b). Economically,  
616 obtaining recovered polymers with acceptable quality by markets (close to that of virgin

617 plastics) (Garforth et al., 2004). To meet the needs of material markets for recycled  
618 products, which have a lower price than virgin products, a cost-efficient method of plastic  
619 recycling and upgradation is developed (Drain et al., 1981). Apparently, offsetting the  
620 costs of high-quality recovered polymers through technical progress is the only and  
621 important way.

622

623 The selection of optimum solvents and solvent pairs for extraction is crucial, as well as  
624 the reduction of extraction time and solvent usage (Vandenburg et al., 1997). However,  
625 some organic solvents are hazardous (Prat et al., 2016), which limits their usage.

626 Consequently, choosing low-poisonous and cheaper extractors (e.g., natural solvents,  
627 such as terpene oils) is one of the future directions for recycling polymers. “Green”  
628 solvents are a good choice, for example, SCFs (Knez et al., 2014) and natural solvents  
629 (Noguchi et al., 1998b) gain a growing interest at present. In a word, an efficient  
630 separation of the polymers would powerfully impulse the recycling industry (Martinho et  
631 al., 2012). Another important thing is an efficient and economic recovery system to  
632 recycle the solvents involved in the process of recycling. In the future, the recovery of  
633 waste plastics will certainly soar, considering the fact that the diversity of contaminants  
634 and materials in plastics continuously shrinks (Schlummer et al., 2007a).

635

#### 636 **List of Abbreviations**

ABS acrylonitrile-butadiene-styrene

|             |   |
|-------------|---|
| ACE         | acetone   |
| ASE         | accelerated solvent extraction                                  |
| BFRs        | brominated flame retardants                                     |
| C           | concentration of a solute in the solvent in grams of each liter |
| CL          | chemiluminescence   |
| DCM         | dichloromethane   |
| DSC         | differential scanning calorimetry                               |
| EPS         | expanded polystyrene  |
| FTIR        | Fourier transform infrared spectroscopy                         |
| GC-MS       | gas chromatography–mass spectrometry                            |
| GPC         | gel permeation chromatography                                   |
| HDPE        | high-density polyethylene                                       |
| HIPS        | high-impact polystyrene   |
| HPLC        | high-performance liquid chromatography                          |
| HPLC–<br>UV | liquid chromatography with UV detection                         |
| HSP         | Hansen solubility parameter                                     |
| LDPE        | low-density polyethylene  |

|                   |                                   |
|-------------------|-----------------------------------|
| MAE               | microwave-assisted extraction     |
| MEK               | methyl ethyl ketone               |
| MFI               | melt flow index                   |
| NIR               | diffuse-reflectance near-infrared |
| NMP               | N-methyl-2-pyrrolidone            |
| PC                | polycarbonate                     |
| PET               | Poly(ethylene terephthalate)      |
| PetE              | petroleum ether                   |
| PLE               | pressurized liquid extraction     |
| PMMA              | poly(methyl methacrylate)         |
| PP                | polypropylene                     |
| PS                | polystyrene                       |
| PVB               | polyvinyl butyral                 |
| PVC               | polyvinyl chloride                |
| RED               | relative energy difference        |
| SAN               | styrene-acrylonitrile             |
| SCCO <sub>2</sub> | supercritical CO <sub>2</sub>     |

|            |   |
|------------|---|
| SCFs       | supercritical fluids                              |
| SEM        | scanning electron microscopy                      |
| SFE        | supercritical fluid extraction                    |
| TBBP<br>A  | tetrabromobisphenol A                             |
| TGA        | Thermogravimetric analysis                        |
| THF        | tetrahydrofuran                                   |
| UAE        | ultrasonic-assisted extraction                    |
| WEEE       | waste electrical and electronic equipment         |
| XPS        | extruded polystyrene                              |
| $\delta_D$ | interaction: dispersion forces                    |
| $\delta_P$ | permanent dipole–permanent dipole forces          |
| $\delta_H$ | hydrogen bonding                                  |
| $R_a$      | distance between the polymer and the solvent      |
| $R_0$      | radius of the polymer solubility sphere           |
| $\rho$     | density of the fluid (gas) in grams of each liter |

637

638 **Acknowledgments**

639 This work was financed by the Guangdong Science and Technology Plan Public Welfare

640 Project (2016A020221003). We also thank the anonymous reviewers for their  
641 constructive comments.

642

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1006 **Table 1**  
 1007 Common solvents for target polymers used in the dissolution/reprecipitation method.

| Polymer | Strong solvents                                 | Weak solvents                    | Experimental conditions   | References                                      |
|---------|---|----------------------------------|---|---|
| PS      | DCM<br>Toluene                                  | methanol                         | 5-10 g/100 mL solution was obtained, and the experiment temperature was 100 °C.   | (Achilias et al., 2009a)                        |
| PS      | Toluene<br>Xylene                               | n-hexane<br>Methanol             | 1 g PS was dissolved in 20 mL solvent with heating for 30 min, reprecipitated, and dried at 89°C for 24 h.  | (Achilias et al., 2009b)                        |
| PS      | Limonene<br>Terpinene<br>Cymene<br>Phellandrene | -                                | The solution (~0.25 g/mL) in glass tubes was obtained at 25°C.  | (García et al., 2009a;<br>García et al., 2009b) |
| PS      | Cyclic monoterpenes                             | Water                            | 0.2 g PS film was dissolved in 2 cm <sup>3</sup> cyclic monoterpenes with strokes of 120 min <sup>-1</sup> , then water (50 cm <sup>3</sup> ) was added.  | (Shikata et al., 2011)                          |
| PS      | D-limonene                                      | -                                | A volume of 5 cm <sup>3</sup> limonene dissolved EPS (125 cm <sup>3</sup> ) in 3 min.   | (Noguchi et al., 1998b)                         |
| PS      | Benzene/toluene                                 | water                            | PS was dissolved in benzene or toluene, and 3 times of water was added with stirring (800 rpm), which was dried in the oven at 70°C for 24 h.   | (Kampouris et al., 1988)                        |
| PS      | MEK<br>MEK<br>p-xylene                          | Methanol<br>n-hexane<br>n-hexane | The PS solution (0.25-0.3 kg/L) was filtered (200-150 μm) under pressure (0.2-0.3 MPa, 20 °C), and a non-solvent (4-10 times volume of solvent) was added with stirring for 30 min, followed by centrifugation. | (Kampouris et al., 1987)                        |
| PC      | DCM   | DCM/ACCE (v/v=1)                 | The e-waste plastic was dissolved in 50/50 (vol %) ACE/DCM at room temperature, and PC was precipitated.  | (Weeden et al., 2015)                           |
| PC      | DCM   | Methanol                         | 5-10 g/100 mL solution was obtained, and the experiment temperature was 50 °C.  | (Achilias et al., 2009a)                        |
| PE      | Xylene  | Propanol                         | 30 L xylene was added into a mixture of 3 kg PE and 3 kg PP with  | (Pappa et al., 2001)                            |

|     |                     |                        |   |                                   |
|-----|---------------------|------------------------|---|-----------------------------------|
| PE  | Xylene              | n-hexane<br>methanol   | stirring for 1 h at 85 °C, and PE was dissolved, precipitated by 90 L propanol, and dried at 80 °C for 6 h. 1 g PE was dissolved in 20 mL solvent with heating (100 °C) for 30 min, reprecipitated, and dried at 89°C for 24 h. | (Achilias et al., 2009b)          |
| PP  | Xylene              | ACE                    | The solution of 0.15 kg/L was obtained at 135 °C and filtered under pressure through a 20-70 µm filter. ACE was added to precipitate and wash.  | (Poulakis and Papaspyrides, 1997) |
| PP  | Xylene              | n-hexane               | 1 g PP was dissolved in 20 mL solvent with heating (140 °C) for 30 min, reprecipitated, and dried at 89°C for 24 h.   | (Achilias et al., 2009b)          |
| PP  | Tetrachloroethylene | ACE                    | 300 g PP was dissolved in 3 L Tetrachloroethylene by heating at 121 °C for 15 min and then became a gel in 2 L acetone.   | (Murphy et al., 1979)             |
| PET | Benzyl alcohol      | methanol               | 1 g PET was dissolved in 20 mL solvent with heat (180 °C) for 30 min, reprecipitated, and dried at 89°C for 24 h.   | (Achilias et al., 2009b)          |
| PET | NMP                 | -                      | NMP was used to remove impurities at 130 °C, and then PET was dissolved at 160 °C.  | (Vane and Rodriguez, 1992)        |
| PET | NMP                 | n-octane +<br>n-hexane | 0.1 kg PET bottle was dissolved in 0.5 L NMP to form a solution of 0.02 kg/L at 165 °C with stirring for 90 min. 1L n-octane and 2 L n-hexane were added with stirring, and the recovered polymer was dried at 90 °C for 14 h.  | (Poulakis and Papaspyrides, 2001) |
| ABS | ACE                 | Methanol               | 5-10 g/100 mL solution was obtained, and the experiment temperature was 25 °C.  | (Achilias et al., 2009a)          |
| ABS | ACE                 | -                      | ABS was dissolved to form a solution for 40 min (0.25g/mL ACE) at room temperature  | (Arostegui et al., 2006)          |
| PVC | 85/15               | -                      | Up to 15% cyclohexanone and   | (Sperber                          |

|     |                      |          |   |                          |
|-----|----------------------|----------|---|--------------------------|
|     | xylene/cyclohexanone |          | temperature range of 115-125 °C were employed to separate polyolefin, PS, and PVC.  | and Rosen, 1976)         |
| PVC | Cyclohexanone        | n-hexane | 0.30 kg PVC /L cyclohexanone and 1/7 in volume solvent/nonsolvent were used. PVC was dissolved with stirring and heating for 15-60 min filtered (0.2-0.3 MPa), and precipitated at room temperature with stirring (50 rpm). | (Kampouris et al., 1986) |
| PVC | DCM<br>Toluene       | methanol | 1 g PVC was dissolved in 20 mL solvent with heating for 30 min, reprecipitated, and dried at 89 °C for 24 h.  | (Achilias et al., 2009b) |

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1009 **Table 2**

1010 General comparison of solvent extraction with primary mechanical recovery.

|               | Solvent extraction  | Primary mechanical recovery   |
|---------------|---|---|
| Procedures    | (1) Cut and remove the pollutant and impurity.<br>(2) Dissolve to the highest possible concentration.<br>(3) Re-precipitate the polymer in solvents by adding nonsolvents (add supercritical fluids to extract solvents)<br>(4) Filter, wash, and dry the obtained polymer<br>(5) Separate and recover solvent/nonsolvent (solvent/supercritical fluids). | (1) Shred (grind) plastic in a suitable form<br>(2) Wash the plastics by water<br>(3) Agglutinated by pigments and additives<br>(4) Extrusion<br>(5) Quenching<br>(6) Granulation |
| Advantages    | (1) Obtained in accepted form, such as granules and powder.<br>(2) Remove the additives and insoluble contaminants.<br>(3) No further degradation occurs except heating for a fully dissolution.<br>(4) The properties of the recycled product are competitive compared with virgin products.<br>(5) A massive decrease in the bulk volume.               | (1) The properties of the recycled product are competitive compared with virgin products.<br>(2) Simple operation   |
| Disadvantages | (1) Relatively high technical requirements<br>(2) Relatively high costs   | (1) Degradation of recovered product<br>(2) Limited applications  |

1011

1012 **Table 3**

1013 Description of assessment techniques for recovered polymers.

|                    | Descriptions  | Applications  |
|--------------------|---|---|
| FT-IR              | It analyzes possible oxidative degradation and quantify the relative polymer contents in blends | Specific functional groups<br>Changes in the chemical structure<br>Possible oxidative degradation                 |
| DSC                | It provides thermograms of polymers   | Kinetics of crystallization<br>Degree of crystallinity<br>Apparent crystallization<br>Compatibility of the blends |
| Raman spectroscopy | The technique to infrared spectroscopy  | Analysis of conformation, tacticity, orientation, crystallinity, and functional groups                            |
| TGA                | It is used for thermogravimetric analysis   | Thermal degradation studies   |
| GPC                | A kind of size exclusion chromatography   | Determination of relative molecular weight and distribution of molecular weights of polymers                      |
| HPLC               | Separation, identification, and quantification of each component in a mixture                   | Determination of concentration and identification of species  |
| CL                 | It analyzes the emission of light from the chemical reactions                                   | Monitoring oxidation reactions  |
| GC-MS              | It identifies substances of a sample integrating gas-chromatography and mass spectrometry       | Identification of elements and species  |
| MFI                | A measure of flow of molten polymers  | Determination of melt viscosity, molecular weight (indirectly)  |
| SEM                | It analyzes the blend morphology of polymers  | Morphology of fracture surfaces, reactive and physical blends   |

1015 **Table 4**

1016 Extraction techniques of additives (including BFRs) in waste plastics.

|                    | Description  | Advantages   | Disadvantages                          |
|--------------------|--|--|--|
| PLE                | The solvent extraction is accelerated by higher pressures and temperatures above normal boiling points | Fast, high recovery yield, automated   | High cost of equipment, less selective |
| MAE                | The solvents are heated by microwave energy  | Lower solvent consumption, exact reaction control in temperature and pressure, less time consuming | Expensive, requires additional process |
| UAE                | The separation is powered by ultrasound  | Cheap, easy to use, effective, multi-extraction  | Not always effective                   |
| SFE                | Supercritical fluids are employed under relatively high pressure and temperature                       | High extraction efficiency, low toxicity, nonexplosive properties                                  | Relatively expensive                   |
| Soxhlet extraction | The target compounds are extracted by the solvent, and the other materials are insoluble               | Simply operation, low cost   | Slow, solvent consuming                |

1018 **Figure captions:**

1019 **Fig. 1.** Global cumulative generated plastic waste and plastic disposal(Geyer et al., 2017).

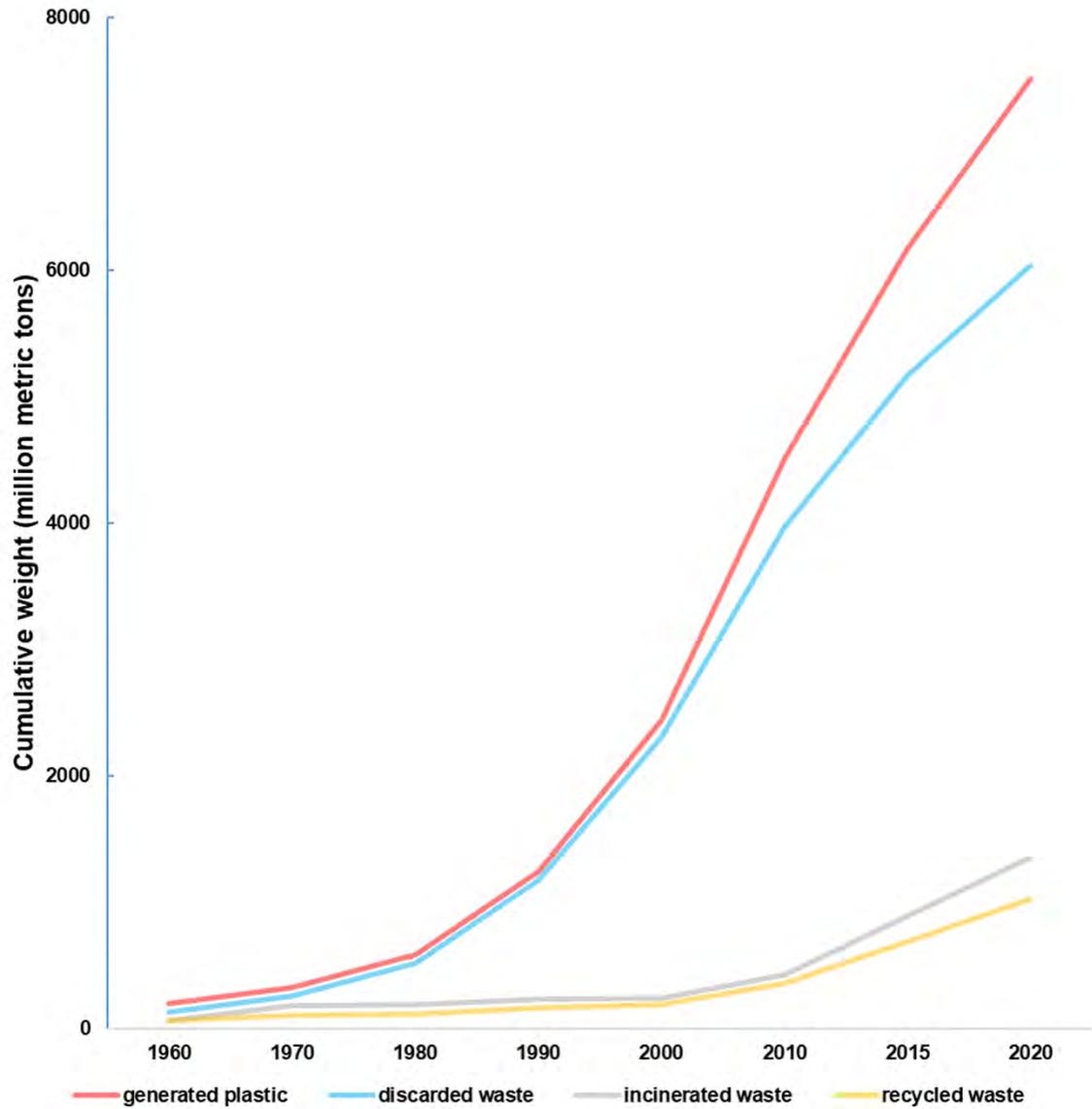
1020 **Fig. 2.** Composition of surface layers during the dissolution process.

1021 **Fig. 3.** Hansen solubility sphere for the specific polymer (in yellow) along with “strong  
1022 solvents” (points in yellow) and “weak solvents” (points in blue).

1023 **Fig. 4.** Schematic drawing of the dissolution/precipitation technique.

1024 **Fig. 5.** Schematic drawing of the supercritical fluid extraction recycling.

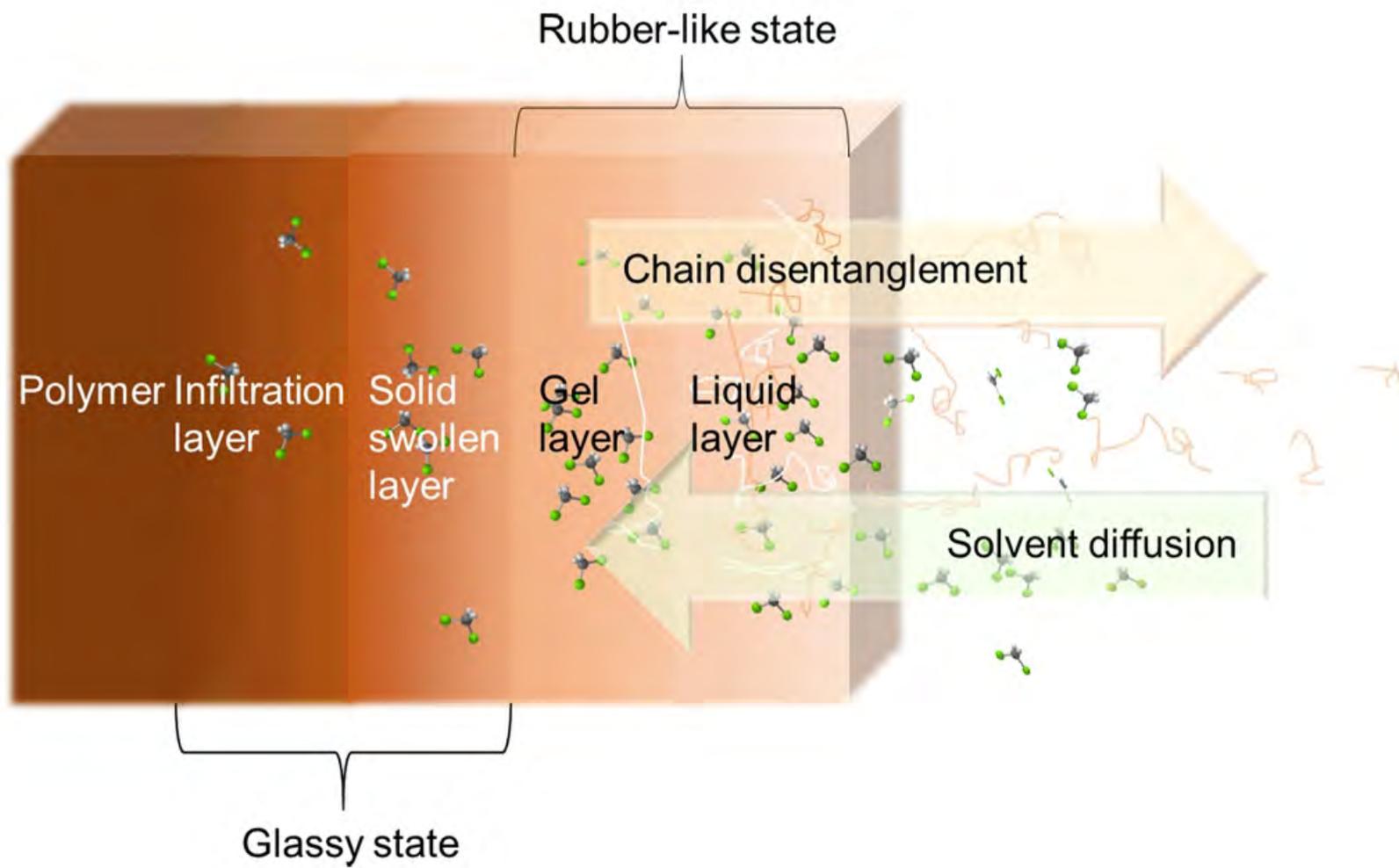
1025 **Fig. 6.** Mechanical degradation mechanisms during the recovery processes (increased  
1026 recovery is marked in red and decreased recovery is marked in blue).



1028

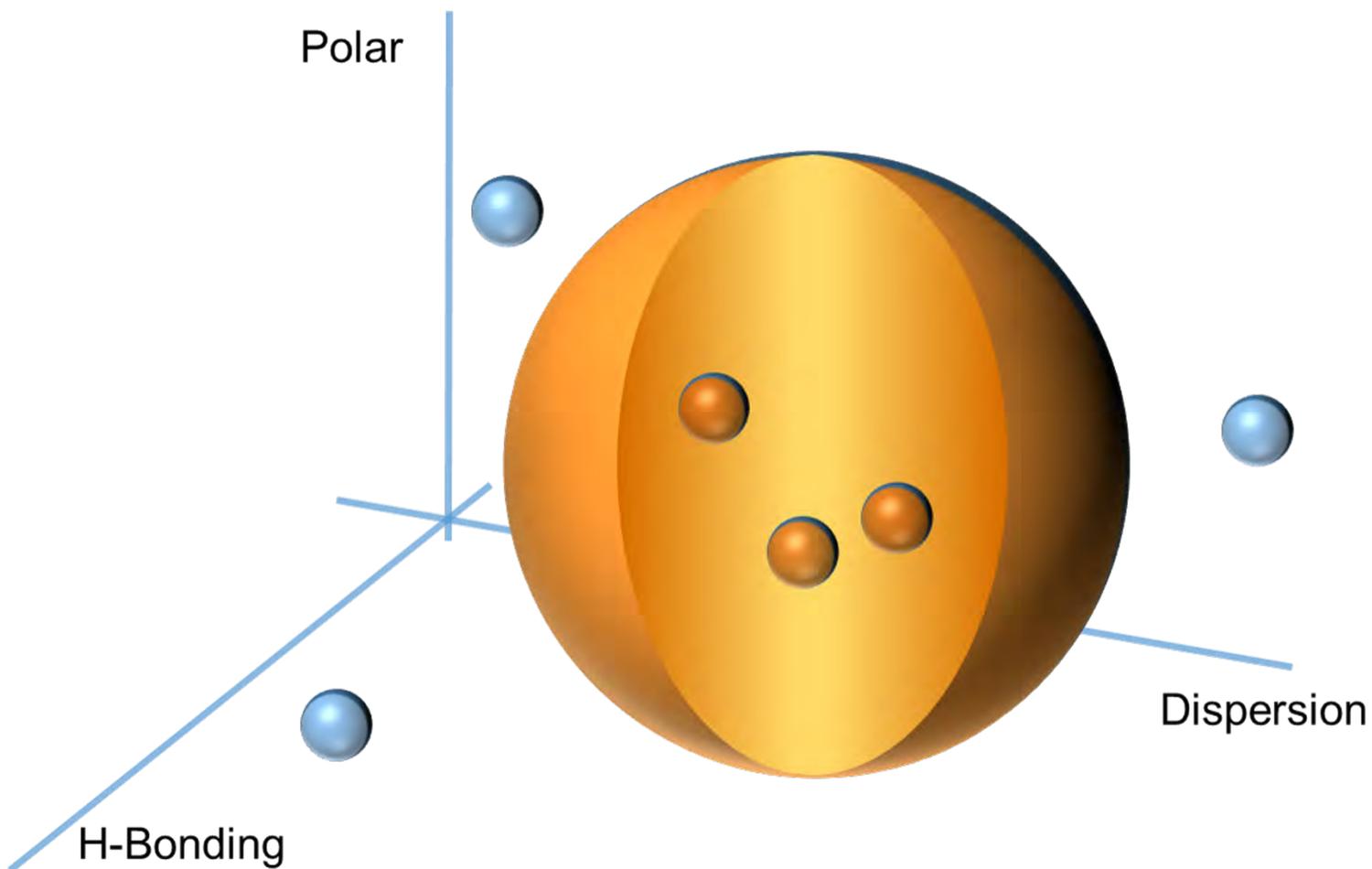
1029 **Fig. 1.**

1030



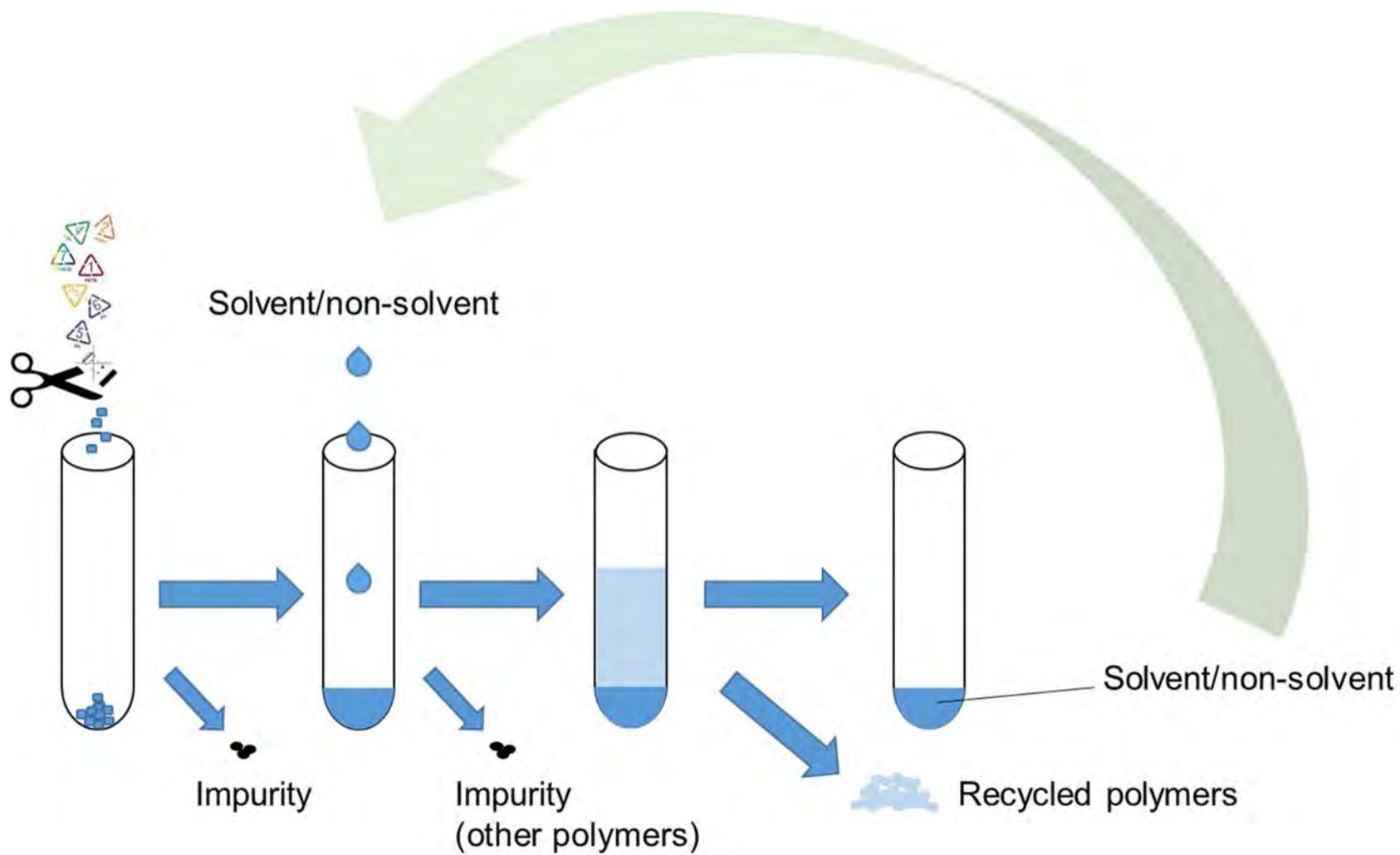
1031

1032 **Fig. 2.**



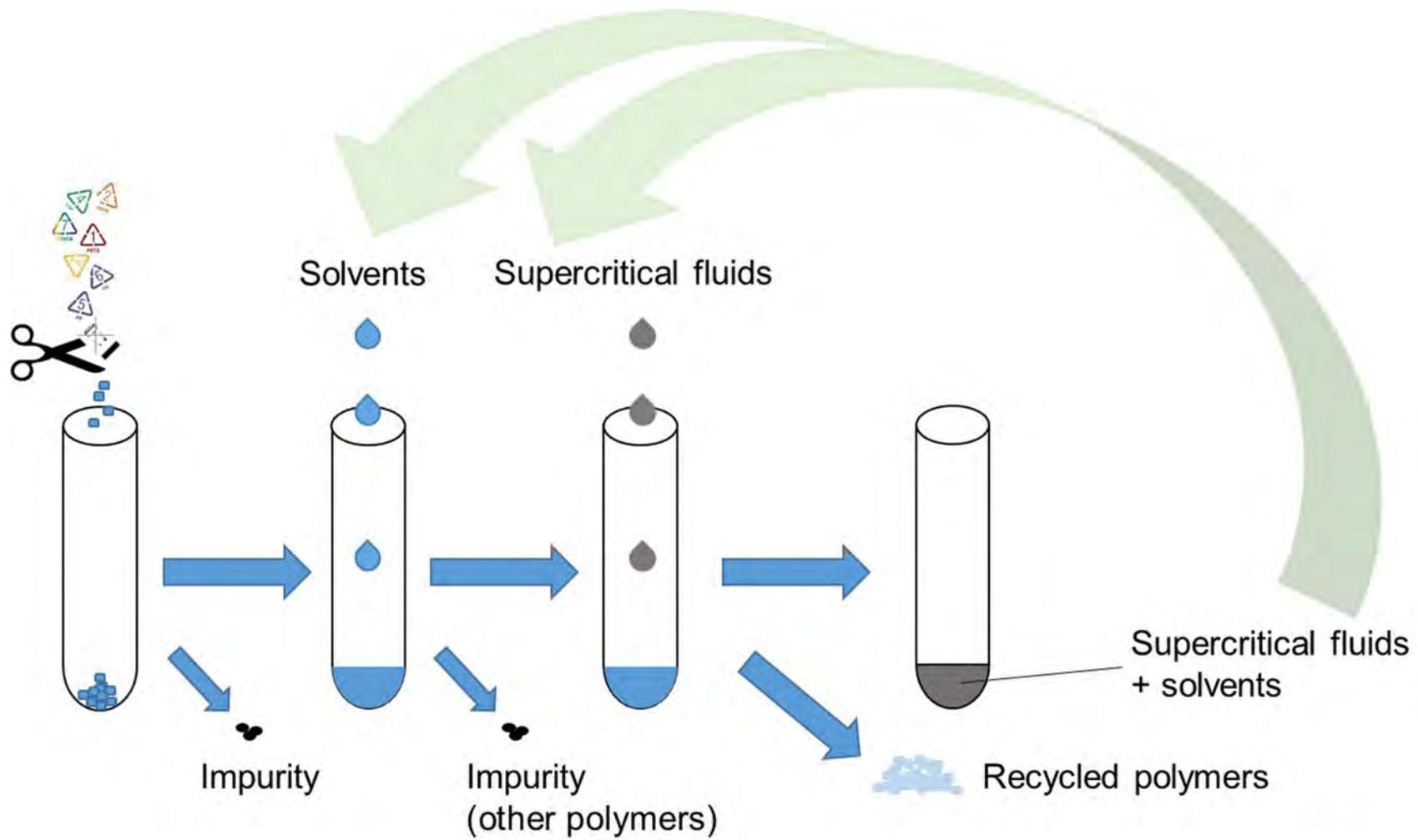
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**Fig. 3.**



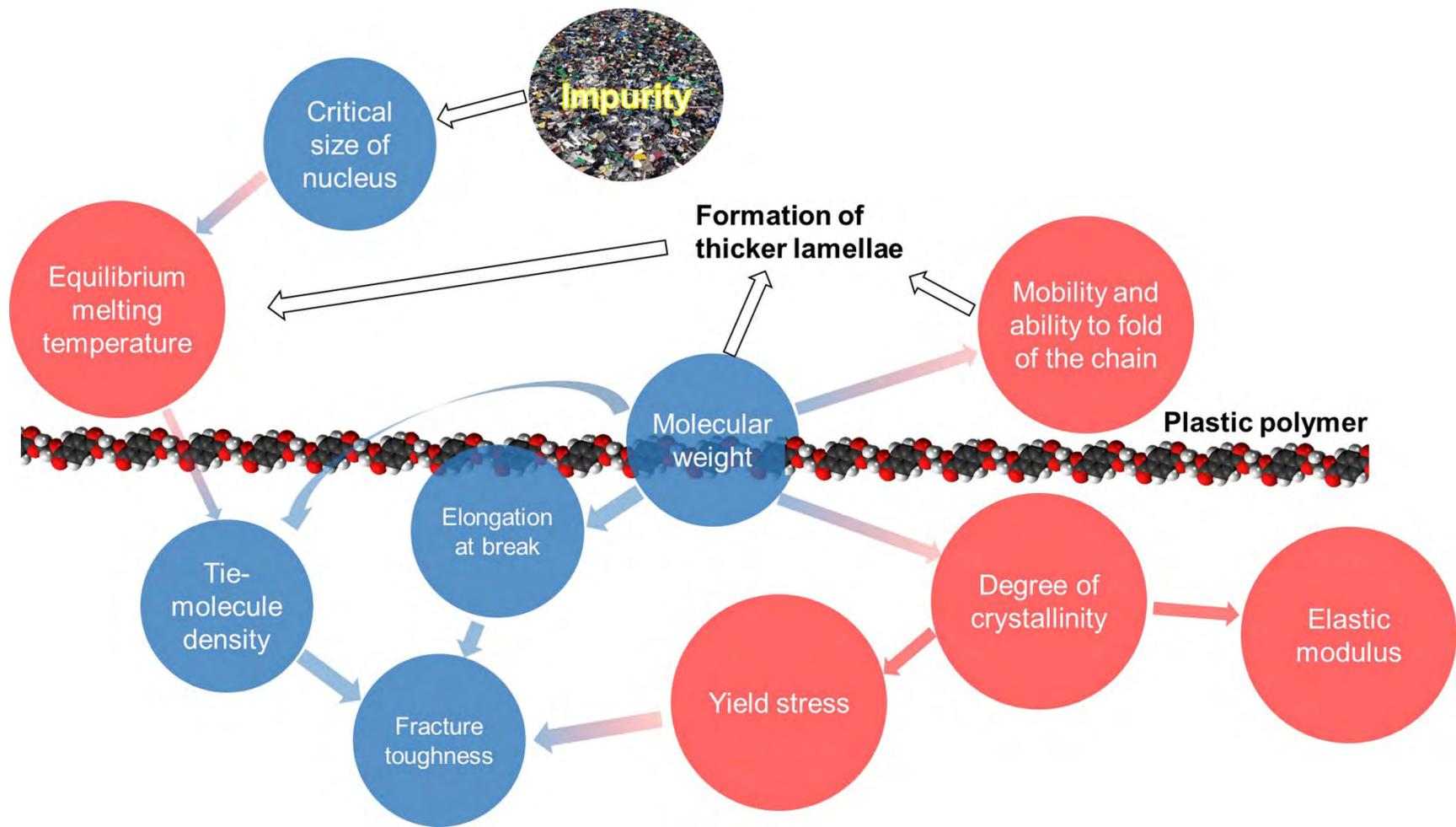
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1036 **Fig. 4.**



1037

1038 **Fig. 5.**



1039

1040 **Fig. 6.**

### Research highlights

- Solvent extraction is a promising method to separate waste mixed plastics.
- The method is potentially applied for recycling mass-produced plastics.
- The method is environmentally benign and is potentially profitable.