Supporting Information for

Large-scale Computational Polymer Solubility Predictions and Applications to Dissolution-based Plastic Recycling

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Polymer solubility database

An Excel spreadsheet including the complete prediction results of the polymer solubilities in various solvents at multiple temperatures is included as part of this Supporting Information. The spreadsheet includes the compound names, CAS numbers, boiling points, Hansen solubility parameter (HSP) values, SMILES strings and compound classes of the solvents. HSP values are from the HSP handbook.[1] Boiling points and SMILES strings are from COSMObase-1901-BP-TZVP. Compound classes are identified based on the SMARTS substructure matching syntax via Python package RDKit.[2, 3] In this spreadsheet, solubility prediction result for each polymer-solvent system is at two different temperatures: a room temperature (RT) and a higher temperature (T_h), which is defined to be 1 °C lower than the boiling point (BP) of the solvent, with an upper bound of 120 °C ($T_h = \max\{120, BP - 1\}$). Note that some solvents have boiling points lower than the RT, which leads to some "NaN" values. A few polymer-solvent systems are predicted to be fully miscible at the given temperature, which is labeled as "M" in the datasheet.

Discussion on related studies

Here, we summarize some studies related to the topics of dissolution-based plastic recycling, solvent screening for polymers, and solubility prediction methods. This summary includes studies in both industry and academia. We also provide some examples of current benchmarks for solvent screening and discuss some limitations of the various prediction methods.

Literature reports of solvents/non-solvents for common polymers. **Table S1** includes a selected list of known solvent and non-solvents for some common polymers studied in this work. While valuable, this list of solvents it is not sufficient for designing selective dissolution processes complex, multicomponent input streams; when there are multiple polymers present in an input stream, finding a selective solvent only using literature information is challenging. Moreover, this list does not consider a wide range of temperatures unlike the computational predictions performed in this work.

Table S1. A selected list of solvents and non-solvents for the polymers considered in this work.

Polymer	Solvents	Nonsolvents	References
EVOH	acetamide DMF DMSO (hot) glycerol (hot)	carboxylic acids esters hydrocarbons lower alcohols	4-6
PE	xylene (100 °C) THF toluene 1,2,4-trichlorobenzene	propanol hexane methanol	5, 7-10
PP	benzene diethyl ether tetrachloroethylene (121 °C) xylene (135 °C)	acetone hexane	5, 8, 9
PS	carbon disulfide chloroform cyclohexane (>35 °C) DCM (100 °C)	acetone phenol methanol hexane	5, 9, 11
PET	benzyl alcohol (180 °C) NMP (160 °C) γ-valerolactone DMSO (hot)	aliphatic alcohols hydrocarbons ethers ketones	4, 5, 9, 12
PVC	chlorobenzene DMF MEK THF	hexane methanol acetic anhydride alcohols	5, 9, 13
Nylon 6	DMSO acetic acid chlorophenol *m*-cresol	MEK chloroform esters ethers	5, 14
Nylon 66	formic acid chloral hydrate (RT) acetic acid benzyl alcohol (120-180 °C)	aliphatic alcohols chloroform diethyl ether hydrocarbons	5, 14

Industrial projects. **Table S2** summarizes some dissolution-based plastic recycling processes being adopted at industrial scale. These processes indicate the feasibility of scaling-up selective dissolution processes, but limited information on the solvents and operating conditions used in these processes is openly available.

Table S2. Representative industrial processes for dissolution-based plastic recycling.

Company	Process description
APK AG (Germany)	Newcycling®: combines mechanical and solvent-based processes to recycle plastic materials such as LDPE/PA films.[15-17]
VinyLoop (Italy)	Solvent-based PVC purification. Launched in 2022 but terminated in 2018 due to challenges in separating hazardous plasticizer additives.[18, 19]
Unilever (U.K.), Fraunhofer Institute (Germany)	CreaSolv®: Solvent-based process to recycle polymers including PP, PS, PVC, ABS and PC from plastic waste (pilot plant opened in Indonesia).[20-22]
Polystyvert (Canada)	PS recycling through dissolution in essential oil.[23]

Computational solvent screening for polymers. As described in the main text, various solubility parameter systems have been developed to predict polymer dissolution behaviors in different solvents. These parameter systems include Hildebrand,[24] Hansen,[1] Kamlet-Taft,[25] Gutmann,[26] and Swain[27] parameters. In particular, Hansen solubility parameters (HSPs) are widely used to guide solvent selection for polymers, and the use of HSPs is a benchmark solvent screening method for polymers.[1, 28-30] Machine learning techniques have also been employed to facilitate solvent screening for polymers. For example, a deep neural network was trained for binary solvents/non-solvent classification; it used over 4500 homopolymers and 24 common solvents and achieved a high accuracy of 93.8%.[31] We present some examples and conclusions about the limitations of these methods in the following sections.

Examples of HSP-based solvent screening. The HSP system assigns each compound three parameters that account for dispersion, polar and hydrogen-bonding forces (δ_D, δ_P and δ_H). Solvent-polymer interactions are measured by their distance (R_a) in the HSP space ($2\delta_D$-δ_P-δ_H space) using Equation S1.

$$R_a^2 = 4\left(\delta_D^{\text{solvent}} - \delta_D^{\text{polymer}}\right)^2 + \left(\delta_P^{\text{solvent}} - \delta_P^{\text{polymer}}\right)^2 + \left(\delta_H^{\text{solvent}} - \delta_H^{\text{polymer}}\right)^2 \qquad \text{(S1)}$$

The solubility of the polymer in the solvent is determined by dividing R_a by the interaction radius of the polymer, R_0. If $R_a/R_0 < 1$, it indicates the polymer will dissolve in the solvent. $R_a/R_0 > 1$ indicates the polymer will not dissolve in the solvent.

Here, we use low density PE (LDPE), dodecane and acetone to illustrate some problems that one may encounter when performing HSP-based solvent screening. The HSPs for these compounds are shown in **Table S3**. The data are extracted from the HSP handbook.[1]

Table S3. Example HSP data.[1] Multiple versions of LDPE were found, so multiple sets of HSPs are reported.

Polymer	HSP data			
	δ_D	δ_P	δ_H	R_0
LDPE (1)	16.3	5.9	4.1	8.2
LDPE (2)	16.5	4.5	0.5	6
LDPE (3)	15.3	5.3	2.5	10.1
dodecane	16.0	0	0	\
acetone	15.5	10.4	7	\

We first note that there are multiple sets of HSP values for LDPE, with widely varying values. These resins may come from different manufacturers and thus have different properties such as crystallinities and molecular weight distributions. Unfortunately, little information on these differences is provided in this literature. Therefore, it is hard for researchers to decide which set of HSPs is most suitable for their specific LDPE resins.

To illustrate potential challenges with solvent screening using HSPs, we present an example of HSP predictions for LDPE. We specifically use dodecane and acetone as example solvents because we experimentally verified that dodecane is a good solvent and acetone is a non-solvent at high temperatures as shown in **Table 3** of the main text. We calculated HSP R_a/R_0 values for the three LDPEs in the two solvents as shown in **Table S4**. The HSPs (which assume room temperature) predict dodecane to be a good solvent for all three LDPEs ($R_a/R_0 < 1$). These calculations are consistent with the high-temperature experimental results. However, two sets of HSPs predict acetone to be a good solvent (marked in red), which is inconsistent with the experimental results, even though the temperature is lower than the temperature at which solubility was measured experimentally. For LDPE (1), R_a/R_0 is lower for acetone than dodecane, suggesting that LDPE should be even more soluble in acetone than dodecane. These results are thus qualitatively different from the experimental findings. It is possible that the resin we used is more similar to LDPE (2) than LDPE (1) and LDPE (3), but such information is difficult to assess prior to solvent screening.

Table S4. HSP R_a/R_0 calculation results for the example compounds. Values in red indicate inconsistency between HSP predictions and high-temperature experimental measurements (**Table 3** of the main text).

	dodecane	acetone
LDPE (1)	0.88	0.68
LDPE (2)	0.77	1.50
LDPE (3)	0.60	0.67

Limitations of existing methods and improvements of our approach. We conclude by discussing the limitations of existing methods and the advantages of our approach in several aspects:

1. Quantitative prediction of polymer solubility. Both the HSP and the machine learning classification methods mentioned above provide qualitative predictions of polymer behaviors in solvents, i.e., they predict that a polymer should either dissolve or not. However, the amount of solvent usage is an important design parameter for dissolution-based processes.[29] The determination of this parameter requires quantitative data on polymer solubility, which is the gap that this work aims to fill.
2. Temperature dependence of polymer solubility. As shown in **Table S1**, the literature reports on known solvents and non-solvents for polymers typically provide only one temperature for the system, or simply assume room temperature.[5, 9] Computational methods also typically assume room temperature.[28, 31] However, operation temperatures are also critical considerations in selective dissolution and temperature-induced precipitation processes.[32, 33] HSPs at other temperatures can be calculated based on room temperature HSPs and thermal expansion coefficients of the compounds,[1, 28] but the qualitative nature of HSP predictions still limits its ability to provide temperature-dependent information on quantitative polymer solubilities. Our approach, however, can predict the full temperature-dependent profile of polymer solubility in various solvents.
3. Solvent mixtures. The solvent screening methods above are mostly designed for pure solvents. In practical applications, a solvent mixture may be useful in terms of solubility, selectivity, viscosity, boiling temperature (bubble point), etc. For example, in our previous study, a DMSO/water mixture was designed to recover EVOH from a multilayer plastic film and a THF/DMF mixture was designed for selective PETG dissolution.[32] Therefore, predicting polymer solubility in solvent mixtures can enable the design of solvent systems in a larger search space. Although solubility predictions in this work are for pure solvents, our proposed workflow can also be applied to solvent mixtures with trivial modifications, as shown in our previous work.[32]
4. Polymer types and properties. As shown in an example, there can be multiple versions of the same kind of polymers in the HSP database. In reality, the same polymers purchased from different suppliers can have different properties such as crystallinities and molecular weight distributions. The solubility of these resins could differ greatly. In this work, we address this problem by using an experimentally measured solubility for each polymer as a reference input to the computational model so that the solubility prediction has a single resin-specific calibration. We do note, however, that this experimental calibration is also a limitation of our approach as we do not explicitly include molecular weight or the degree of crystallinity as input parameters, although HSPs also have the same limitation. Future work is needed to explicitly incorporate these parameters in our computational workflow without experimental input.

Detailed experimental procedures

The handling of polymer solutions in this work can sometimes be challenging. Here, we summarize some notes about the stirring, filtration, and precipitation procedures used during the experimental measurements.

Stirring. All experiments were performed at lab-scale within three-neck flasks. The amount of solvent used in each experiment was 30-40 g.

- In experiments to measure polymer solubilities, the viscosity of the solution can get high as the concentration of dissolved polymer increases. If the system became so viscous that the magnetic stir bar could not spin smoothly, we stopped adding more polymer and used the current concentration as a lower limit of the polymer's solubility, following the same approach as in our previous studies.[33, 34]
- In the polymer separation case studies, the viscosity of the system was often low because excess solvent was used. Therefore, the solutions could be easily stirred with the magnetic stir bar.

Filtration. There were two types of filtration performed in our experiments:

- Hot filtration with a stainless wire cloth. This filtration procedure was used to separate undissolved polymer(s) from solution in the separation case studies. The stainless wire cloth used in this work had an opening size of 0.0277 inch and an open area of 44.2%. This cloth was selected based on the size of the polymer pellets. Note that the undissolved PS resin in case 1 is in a powder form, but it aggregates during the experiments and thus can still be filtered by the stainless wire cloth. Compared to regular filtration with filter paper, filtration with the stainless wire cloth is much faster, which minimizes the precipitation of the dissolved polymer. In addition, excess solvent was used during the experiments performed for the case studies to reduce the polymer concentration, which avoids immediate polymer precipitation during filtration after the heat is removed.
- Vacuum filtration with a Büchner funnel. This filtration procedure was performed after the precipitation step to obtain the precipitated resins. This filtration uses filter paper with 11 μm pore size. Note that some solutions may cause the filter paper to break easily, as described in case 2. Therefore, caution is needed in this process and the usage of alternative solvents or the addition of another solvent may also be needed.

Precipitation. We used two different methods to precipitate the dissolved polymers:

- Adding a non-solvent (case 1, 2 and 3). Room temperature non-solvents were added to hot solutions to precipitate dissolved polymers. The precipitated resins were then filtered (as described above) and dried in a vacuum oven at 100 °C. Note that the drying temperature should not exceed the melting temperature of the resins, otherwise the resins may melt and adhere to the filter paper.
- Evaporation (case 4 and 5). To compare the yields of case 4 and case 5, we used evaporation to precipitate the polymers in a vacuum oven. To avoid solvent bumping, the temperature was increased gradually until reaching a final temperature of 100 °C.

Polymer separation sequencing and solvent screening

As shown in main text **Figure 4**, our program first generated all possible separation sequences for the polymer mixture under the assumption that only one polymer is to be selectively dissolved in each step. It then provides ranked lists of solvent candidates for all steps in all separation sequences. Only solvents that meet the following criteria are included in the ranking:

1. The boiling point of the solvent must be at least 25 °C;
2. The solubility of the target polymer (the one to be selectively dissolved) at T_h is at least 5 wt%;
3. The solubility of the target polymer in the solvent at RT is at most 10 wt%;
4. The solubility of other polymer(s) in the solvent at T_h is at most 10 wt%;

Here, “target polymer” and “other polymers” refer to different resins in different sequences and steps, thus the set of eligible solvents may also differ. Note that the value thresholds of these rules are quite loose and they do not guarantee selective dissolution of the target polymer. Therefore, the program will then rank these solvents in descending order by their selectivity score, which is defined as target polymer solubility minus average solubility of other polymers at T_h. As a result, the top-ranked solvents will have the largest solubility difference between target polymer and other polymers at T_h, thus it is likely to achieve the selective dissolution of target polymer. We also want to note that this program does not directly provide precipitation strategy for dissolved polymers. This is because precipitation is often less challenging and can be carried out in a variety of ways, as shown in the **Table 5** of the main text.

Case 1: Mixture PE/PS, Sequence PE→PS

In this case study, the physical mixture of PE/PS was separated by selective dissolution of PE in dodecane at 120 °C. Room temperature isopropyl alcohol was then added as a non-solvent to precipitate the dissolved PE. **Figure 5** of the main text shows photos and Fourier transform infrared spectroscopy (FTIR) spectra of the virgin and recovered resins. As shown in the photos, the morphologies of the recovered resins changed: the PE resin changes from pellets to flakes while the PS resin changes from a powder to an aggregate. However, the consistent FTIR results confirms the purity of the recovered resins.

We also performed an experiment that used a different non-solvent. As **Figure S1** shows, the dissolved PE was precipitated by adding room-temperature water. Note that water is not miscible with dodecane, so the precipitation of PE was mainly attributed to the temperature change of the system. We also observed a similar morphology change of the resins, and verified the purity of the recovered resins through FTIR characterization. The yields of the recovered PE and PS are 93.26% and 109.75%, respectively. The yield of PS is slightly higher than 100%, which is possibly attributed to its physical aggregation during the contact with the solvent; some solvent might have been retained within the aggregated PS resin, leading to a mass increase.

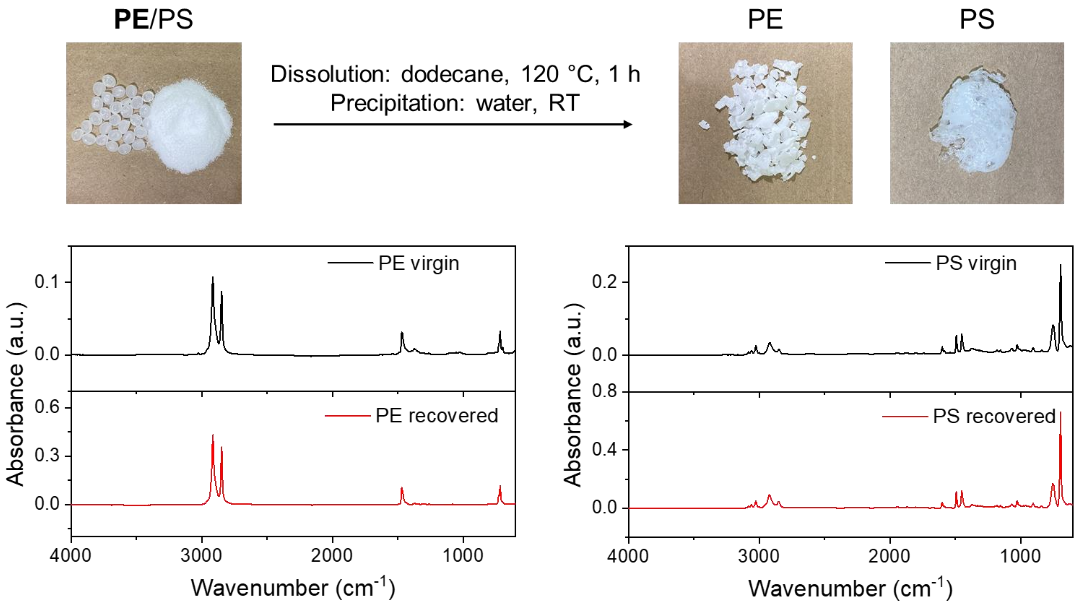

Figure S1. Separation result of case 1 using an alternative precipitation method.

Case 2: Mixture PE/PS, Sequence PS→PE

In this case study, the physical mixture of PE/PS was separated by selective dissolution of PS in ethyl acetate at 75 °C. As for the precipitation of dissolved PS, we observed in a few preliminary experiments that when water was used as the non-solvent, it often made the filter paper break in the following filtration process. We speculated that the mixture of ethyl acetate and water could weaken the tensile strength of the filter paper. Therefore, we selected isopropyl alcohol as the alternative non-solvent, since it is another common lab solvent in which PS and PE are computationally predicted to be insoluble. With this compound, the precipitation and filtration turned out to be successful. As shown in **Figure S2**, the morphology of PE is unaffected, while PS resin changed from powder to a foam-like form. The purity of recovered resins was verified by FTIR spectra.

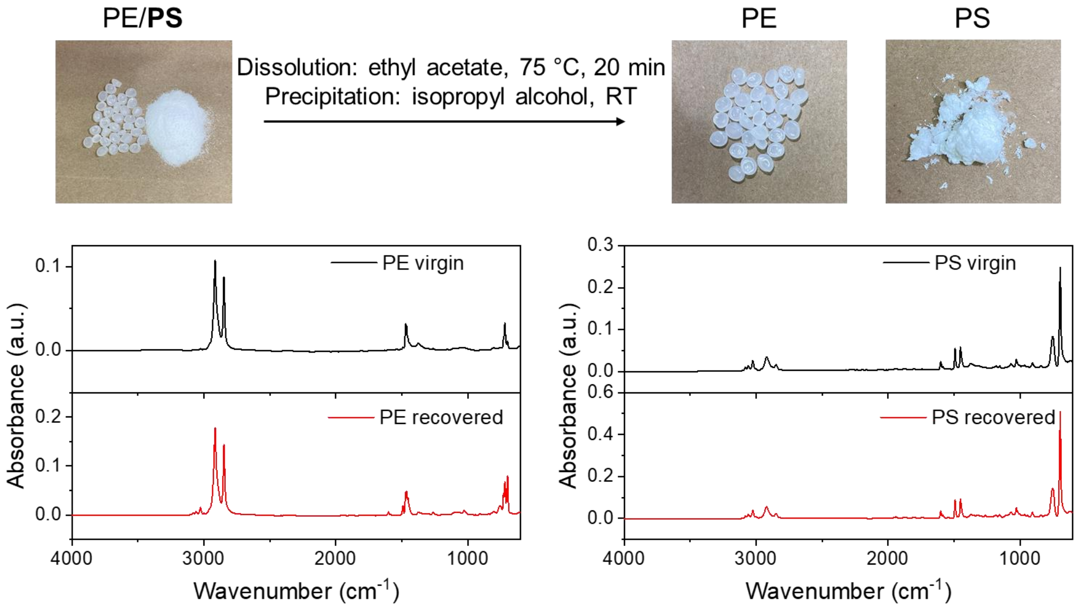

Figure S2. Separation result of case 2.

Case 3: Mixture PVC/PET, Sequence PVC→PET

In this case study, the physical mixture of PVC/PET was separated by selective dissolution of PVC in THF at 65 °C. Room temperature water was then used as the non-solvent for precipitation. **Figure S3** shows the photo and FTIR spectra of virgin and recovered resins. As shown in the photos, the morphology of PVC changed, while the PET resin was unaffected. The consistent FTIR result shows the purity of the recovered resins.

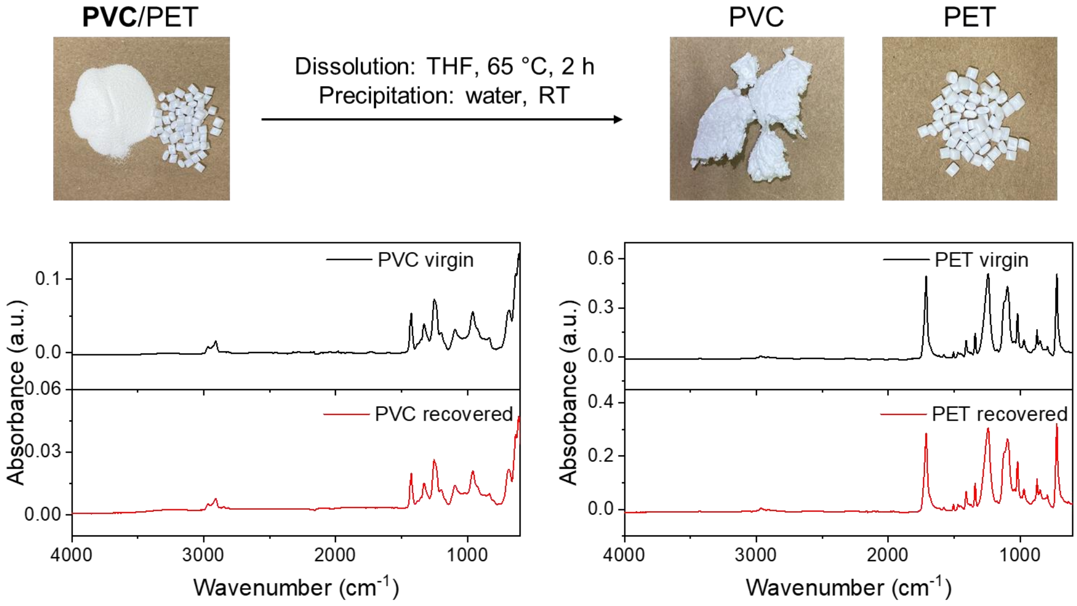

Figure S3. Separation result of case 3.

Case 4: Mixture EVOH/PP/PET, Sequence EVOH→PP→PET

In this case study, the physical mixture of EVOH/PP/PET was separated by first dissolving EVOH in ethylene glycol at 120 °C, then dissolving PP in THP at 88 °C. **Figure S4** shows the photo and FTIR spectra of virgin and recovered resins. In this experiment, we found that the yield of PP is low (78.3%) and we observed an undissolved solid which clearly differs from the PET resin (**Figure S4**). FTIR spectra suggest that the undissolved solid is a mixture of PP and EVOH (**Figure S5**). We speculate that some EVOH and PP agglomerate in the presence of ethylene glycol at the first step and remain undissolved throughout the remaining selective dissolution process. This motivates the experiment of another separation sequence for the mixture, which is the following case 5. Note that in case 4 and 5, the precipitation of dissolved polymers is achieved via evaporation. The purpose of using evaporation is to obtain all the dissolved resins so that we can compare the yields of these two separation sequences.

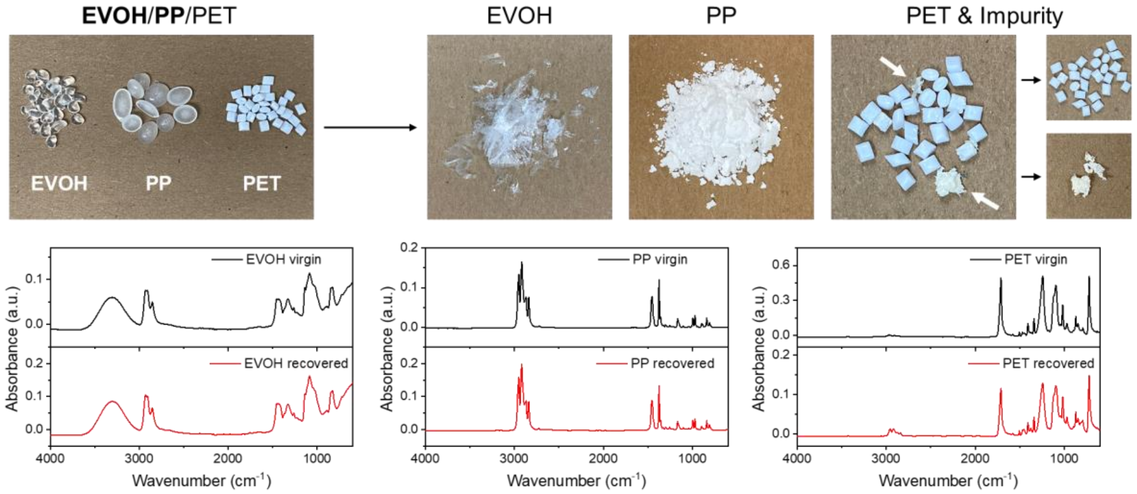

Figure S4. Separation result of case 4. The white arrows in the photo of recovered PET point to the impurities.

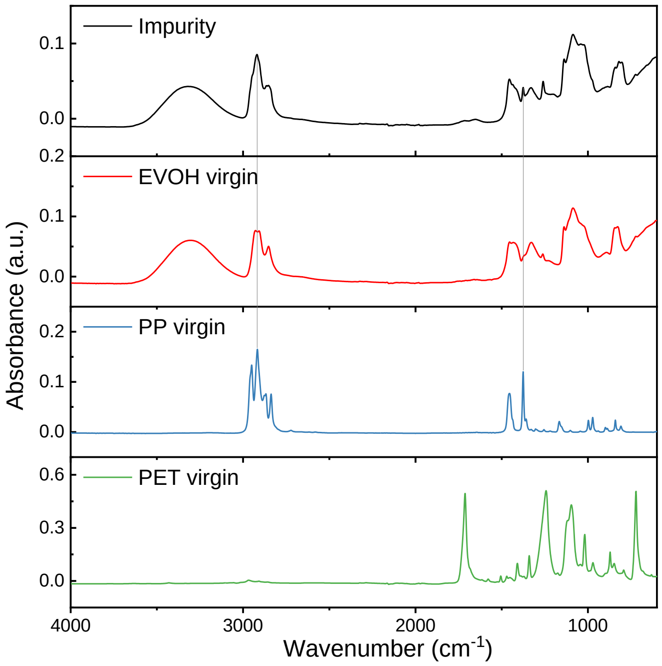

Figure S5. FTIR analysis of the undissolved solid impurity in case 4. The spectrum of the impurity is mainly similar to that of EVOH virgin. The vertical lines showed two peaks that indicate the existence of PP in the solid. This result suggests that the undissolved solid impurity is a mixture of EVOH and PP resins.

Case 5: Mixture EVOH/PP/PET, Sequence PP→EVOH→PET

In this case study, the physical mixture of EVOH/PP/PET was separated by first dissolving PP in THP at 88 °C, then dissolving EVOH in ethylene glycol at 120 °C. The solvents here are exactly the same as that of case 4, only the dissolution sequence is different. In this experiment, we observe no undissolved solid and the yields for all three polymers are excellent. **Figure S6** shows the photo and FTIR spectra of virgin and recovered resins. We note that PET was recovered as pellets because it is last in the separation sequence and hence was not dissolved, so its morphology was unaffected.

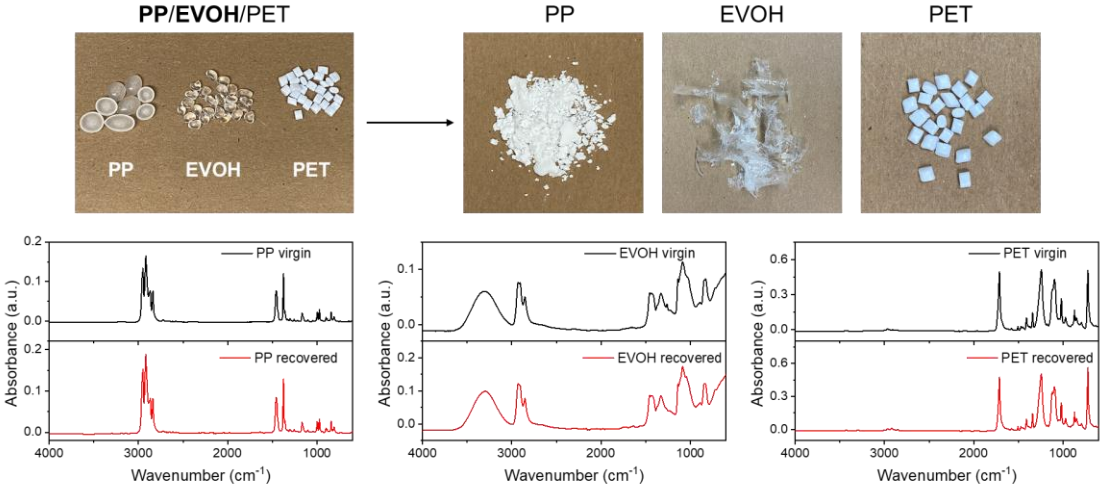

Figure S6. Separation result of case 5.

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