README Documentation for Computational Design

Recycling of multilayer plastic packaging materials by solvent-targeted recovery and precipitation

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1 Description

1.1 Main idea

In this work, we designed a computational workflow to pre-select solvents for the solvent-targeted recovery and precipitation (STRAP) method. Figure 1 shows the general workflow for selecting solvents. First, Hansen Solubility Parameters (HSP) were used to pre-select solvents that are selective to dissolving each polymer. Then, classical molecular dynamics simulations (MD) were performed for these polymers in solvent environments to capture the polymer configurations in free solution. These configurations were subsequently used for COSMO-RS calculations, which uses the charge densities from *ab initio* calculations to estimate solubilities as a function of temperatures and solvent composition. Each portion of this computational workflow is described in detail to allow for readers to reproduce the computational results.

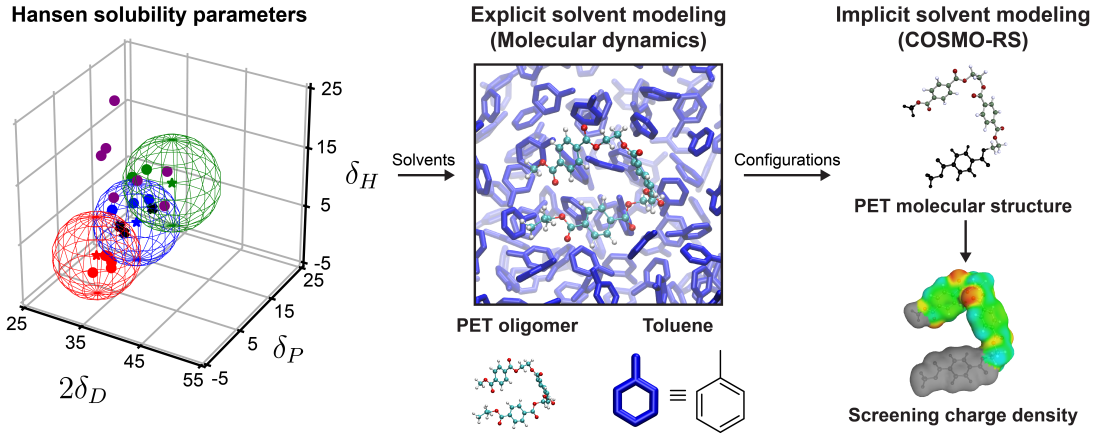

Figure 1: General workflow for the computational design for pre-selecting solvents in the STRAP method. Refer to Figure 2 of the main text for details of the image.

1.2 Data availability

Hansen solubility parameters, classical MD simulations, and COSMO-RS files are available in the Zenodo file: To access the data, download the Zenodo file, and unzip the directory. The command to unzip in Linux terminal is:

```
tar -zxvf NAME.tar.gz
```

where "NAME" is the name of the zipped file.

1.3 Software requirements

The following software is required to run the code:

- Python $\geq$ 3.6 - Used to analyze Hansen solubility parameters and generate MD strutures using Antechamber
- GROMACS 2016 (Version 0) - Used to run MD simulations

- PackMOL (http://m3g.iqm.unicamp.br/packmol/home.shtml) - Solvation tool used to prepare MD systems
- COSMO-RS (COSMOtherm 19) - Used to quantify solubilities with varying temperatures and solvent compositions

2 Hansen solubility parameters

All HSP data are available in the Supporting Information of the main text. Within the main directory, all HSP calculations are performed in:

`STRAP/Hansen_Solubility`

Procedure to extract the results:

- Open the python script used to analyze the HSPs: `extract_hansen.py`
- This script uses input information from `hansen_polymers.csv` and `hansen_solvents.csv`, shown in Figure 2.
- Within `extract_hansen.py`, you may need to change the `MAIN_DIR` variable, which is the directory that the python script is currently located in. Run the python script and it will create a `output` folder, which contains all the output used for the main text.
- Within the `output` folder:
  - `3d_plot.svg`: SVG file used for develop Figure 2a of the main text.
  - `antisolvent.csv`: CSV file containing list of antisolvents
  - `nonselective.csv`: CSV file containing list of non-selective solvents (i.e. selective to more than one polymer)
  - `selective_EVOH.csv`: CSV file containing solvents selective to ethylene vinyl alchohol (EVOH) polymer
  - `selective_PE.csv`: CSV file containing solvents selective to polyethylene (PE) polymer
  - `selective_PET.csv`: CSV file containing solvents selective to poly(ethylene terephthalate) (PET) polymer
  - `solvent_labels_mixed_solvents.csv`: CSV file mixtures of solvents and their classifications
  - `solvent_labels_mixed_solvents.csv`: CSV file pure solvents and their classifications

  Note that some columns may have `ra_by_ro`, which is equivalent to R_a/R_0 in the main text.

hansen_polymers.csv

	A	B	C	D	E
1	Polymer	D	P	H	Ro
2	PE	16.9	0.8	2.8	6.6
3	PS	22.8	5.8	4.3	12.7
4	PET	18.7	6.3	6.7	6.5
5	Nylon 6,6	17.2	9.9	16.5	4.4
6	PP	17.7	2.9	1.2	6.2
7	EVOH	20.5	10.5	12.3	7.3
8	PVDC	19	9.6	9	5.8
9	EVA	18.55	-0.09	3.89	8.15

hansen_solvents.csv

	A	B	C	D
1	Solvent	D	P	H
2	Toluene	18	1.4	2
3	THF	16.8	5.7	8
4	Acetone	15.5	10.4	7
5	1-propanol	16	6.8	17.4
6	1,4 dioxane	19	1.8	7.4
7	NMP	18	12.3	7.2
8	DMF	17.4	13.7	11.3
9	DMSO	18.4	16.4	10.2

Figure 2: Input data into `extract_hansen.py` used to find selective solvents to solubilize polymers. D, P, H, and Ro are δ_D, δ_P, δ_H, and R_0 described in the main text.

3 Classical molecular dynamics simulations

This section describes the classical MD simulations used in the main text. All simulation data is available in the following directory:

`STRAP/Classical_MD`

3.1 Directory structure

The classical MD simulation directory contains the following files:

- `input_files`: input files used for generating MD simulations (*e.g.* MDP files, submission files, *etc.*)
- `polymer_solvent_sims`: simulation folder containing polymer in pure solvents
- `prep_files`: prep files for equilibrating the solvents
- `scripts`: scripts used for generating MD simulations

3.2 Generating new polymers and solvents with Antechamber

All molecules were generated using Antechamber and the Generalized AMBER force fields. Antechamber was accessed using the python module, the installation procedure is described in Listing 1.

```
# CREATE CONDA ENVIRONMENT
conda create -n py36 python=3.6

# INSTALL ACPYPE MODULE
conda install -c acpype acpype

# GO INTO INSTALLATION MODULE AND ACCESS ACPYPE (Below is my own path, please locate
    where your acpype is installed)
cd /home/akchew/anaconda3/envs/py36/lib/python3.6/site-packages/acpype

# GENERAL COMMAND TO RUN ACPYPE
```

```
python acpype.py -di PET_hexamer.pdb -s 86400
# Here, change "PET_hexamer.pdb" to other PDB files
# "-s 86400" means to run Antechamber for an extended period of time (86400 seconds)
# "-di" means to output debugging information and show that the Antechamber is
    running
```

Listing 1: Codes to access Antechamber python module

All polymers were drawn using Spartan 2010 software (alternatives like Avogadro should also work). Solvent molecular structures were generated using the ZINC database (https://zinc.docking.org/), which outputs *.mol2 files for solvents. All outputs from Antechamber are shown in the following directory:
`STRAP/Classical_MD/input_files/acpype_output`

This folder contains four directories:

- `acetone.acpype`: Actone AMBER parameters
- `dmso.acpype`: Dimethylsulfoxide (DMSO) AMBER parameters
- `PET_trimer.acpype`: PET (n=3) AMBER parameters
- `PVA_xy_2_4.acpypee`: EVOH (x=2,y=4) AMBER parameters

3.3 Preparing molecules for MD simulations

Molecules were initially energy minimized with the procedure below:

- Go to scripts folder: `STRAP/Classical_MD/scripts`
- Perform energy minimization by running: `bash prep_molecules.sh PVA_xy_2_4 P24` Here, `PVA_xy_2_4` is the molecule name and `P24` is the 3-letter residue name used in subsequent simulations.
- This script will output energy minimized molecules located in: `STRAP/Classical_MD/prep_files/molecules` For example, within the `acetone` directory, there is:
  - `acetone.gro`: *.gro file with one acetone molecule
  - `acetone.pdb`: *.pdb file with one acetone molecule
  - `acetone.itp`: *.itp file containing atomic charges and bonding information
  - `acetone.prm`: *.prm file containing parameters (*e.g.* dihedraltypes) necessary for MD simulations

3.4 Performing pure solvent simulations

216 solvent molecules were simulated to get estimates of solvent molecular volumes (used to initiate polymer-solvent simulations):

- Go to scripts folder: `STRAP/Classical_MD/scripts`
- Generate 216 solvent simulations by running: `bash prep_solvent_216.sh dmso` This is an example for generating 216 DMSO solvent molecules at 300 K.

- After running the bash script, the equilibrated system is available in the following directory: `STRAP/Classical_MD/prep_files/solvent_equil` Note that you will need to run the 10 ns equilibration by running the `em_equil/submit.sh` code. The Zenodo repository already has the simulations performed with the directories listed:
  - `acetone-216_res-300_K`: 216 acetone molecules simulated at 300 K
  - `dmso-216_res-300_K`: 216 DMSO molecules simulated at 300 K

These solvent systems were used to generate polymer-solvent simulations. Note: You may need to change the path for packmol to where you installed it. Update the `PATH_PACKMOL` variable within `STRAP/Classical_MD/scripts/bin/global_vars.sh` accordingly.

3.5 Performing polymer-solvent simulations

A single polymer in solution was simulated to obtain polymer configurations, using the procedure below:

- Go to scripts folder: `STRAP/Classical_MD/scripts`
- Generate polymer-solvent simulations: `bash prep_polymer_solvent.sh PVA_xy_2_4 dmso` This command will create a simulation of EVOH (x=2,y=4) in the presence of DMSO. Then, run the `submit.sh` script within the output directory, located in: `STRAP/Classical_MD/polymer_solvent_sims`
- The Zenodo folder contains the two MD simulations used:
  - `P_in_S-PET_trimer-acetone-300_K`: PET (n=3) in acetone solution at 300 K
  - `P_in_S-PVA_xy_2_4-dmso-300_K`: EVOH (x=2, y=4) in dimethyl sulfoxide solution at 300 K

  Each directory contains the following:
  - 2 ns NPT equilibration trajectories (*.xtc, *.gro with prefix of "poly_solv_equil")
  - 10 ns NPT production trajectories (*.xtc, *.gro with prefix of "poly_solv_prod")
  - Force field parameters (*.itp, *.prm)
  - Molecular dynamics parameter (MDP) files:
    - Energy minimization: em.mdp
    - NPT equilibration: equil.mdp
    - NPT production: prod.mdp
  - Submission file to perform the simulation: submit.sh

  These MD trajectories were used for subsequent COSMO-RS calculations

4 COSMO-RS calculations

This section describes the COSMO-RS calculations used in the main text. All calculations are available in the following directory:
`STRAP/COSMO-RS`

4.1 COSMO files

The σ-profiles for three EVOH oligomers and six PET dimers are stored in .mcos format in the folder named `cosmo_files`. In the subfolder `COSMO-RS/cosmo_files/Solvents`, the σ-profiles for four solvents (Dihydropyran, GVL, NMP, and Tetrahydrofurfuryl alcohol) that do not exist in the COSMOtherm database are also included in .cosmo format. The enthalpy of fusion and melting temperature data are stored in .vap files.

4.2 Input examples for COSMOtherm

Three command-line version input files for COSMOtherm are included in the folder `/input_examples`. `PE-DMSO1.inp` and `PE-DMSO2.inp` are input files for calculating the solubility of PE in DMSO using method 1 (the heat capacity difference is assumed zero) and method 2 (the heat capacity difference is approximated as $\Delta H_{\mathrm{fus}}/T_{\mathrm{melt}}$ at room temperature, respectively. `EVOH_mixture.inp` is an input file for calculating the solubility of EVOH in a mixture of DMSO and water at room temperature.