Starch composite Hydrogels for Waste-Water Treatment

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1. Abstract

The central goal of the project was to study the interaction between thermo-plastic starch, water, and clay nano-particles in a simulated environment.

We prepared a starch system from Amylose, Amylopectin, Sorbitol and water. The hydrogel system thus prepared underwent equilibration steps and was brought at desired levels of temperature, pressure and density values.

2. Excerpt of the work done in the project

1. To accomplish our task, we are required to make a hydrogel system with percentage composition(w/w) as-
    a. TPS-10%
    b. Water-90%

Avicel 101 nominal concentration (%)	Average cellulose content (wt %)	Average water content based on TGA (wt %)	Calculated hydrogel density (g/cm^3)	Calculated cellulose volume fraction (υ_p)	Calculated volume fraction of water (υ_s)
2	6.3	93.7	1.017	0.044	0.956
3	8.1	91.9	1.023	0.057	0.943
4	9.0	91.0	1.026	0.064	0.936
5	9.4	90.6	1.028	0.067	0.933

Table1. Volume Fraction of Cellulose and Water in Swollen Hydrogels

2. We aimed to prepare the final hydrogel in a cubic box of side length 23 nm equivalent to volume of 12167nm^3.
   First, we need to find the **weight of thermos-plastic starch** using the above data.
   From previous research work done, we had the composition of TPS as –

Compounds	**#mols**
Amylose	90
Amylopectin	42
Sorbitol	4633
Water	256X13 =3328

Table 2. The composition of TPS

Finally, we'll get number of moles of the constituents as 0.23 times the previous one.

*The calculations are given in Appendix

This gives:

Compounds	#mols
Amylopectin	10
Amylose	21
Sorbitol	1066
Water	4X256=1024

Table 3. New Composition of TPS

3. These number of chains of the molecules are packed using the software "Packmol".
   The output is a .pdb file.

   *The procedure is given in Appendix.

4. Now we prepared a correct topology for thermo-plastic starch(TPS) from available coordinate files of
   - Amylose,
   - Amylopectin, and
   - Sorbitol.

   *The procedure is mentioned in the Appendix.

5. Now, simulation runs are to be started.
   First step is solvation of the box. We did this keeping the box size unchanged. (The TPS was already packed such that we didn't needed to change the size before solvation)

   No. of water molecules added – 245,972
   Weight of water molecules added - $7.35X10^{-18}$g
   Percentage of water(w/w) =85%(in the new hydrogel system just prepared) which is close to our expected value of 90%.

6. Secondly, we did energy minimization of the solvated system.

7. It was followed by NVT and NPT steps.
   Temperature=353K (mentioned in nvt.mdp)

   Pressure=1atm(mentioned in npt.mdp)

   *The procedure with commands used during equilibration steps are given in Appendix.

8. After completion of the two equilibration phases, the system was well-equilibrated at the desired temperature and pressure.

9. We are now ready to release the position restraints and run production MD for data collection.

Note: The temperature, pressure, simulation time and other parameters are stored in the .mdp script. The parameters were decided based on discussions.

3. Analysis

3.1 Temperature after NVT step

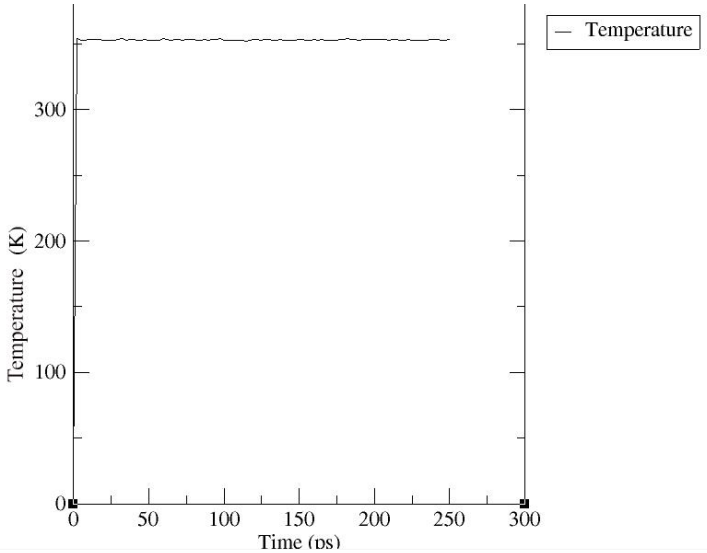

Fig 3.1 Graph of Temperature vs Time

The desired temperature was 353K and from Fig 3.1, the average temperature came out as 352.663K.

3.2 Density(ρ)

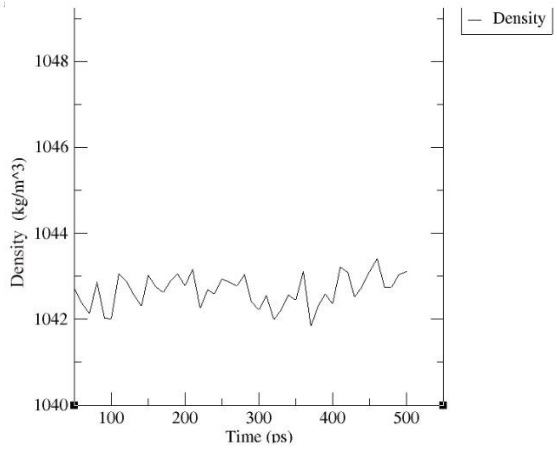

Fig 3.2 Graph of Density vs Time

From Fig 3.2, ρ_{avg} = 1.042g/cm^3 which lies in the expected range (1-1.1 g/cm^3).

3.3 Radius of Gyration*Definition in Appendix

3.3.1 Amylopectin

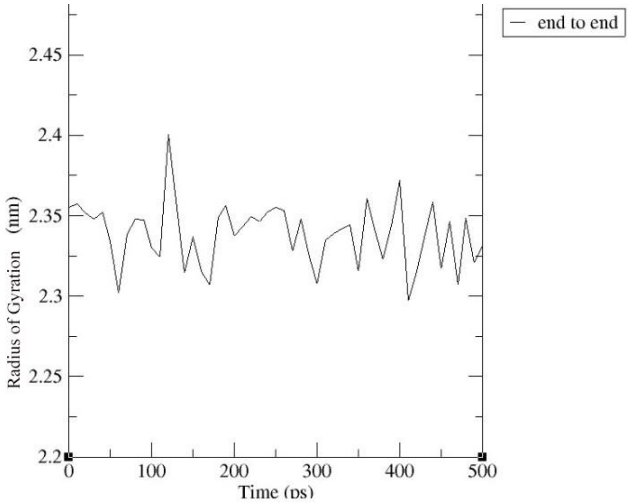

Fig 3.3 Graph of Radius of Gyration of Amylopectin vs Time

From fig 3.3, $R_{g,avg}$ of amylopectin came out to be 2.730 nm. This is close to the $R_{g,avg}$ of amylopectin of Akash system which was 2.5 nm.

3.3.2 Amylose

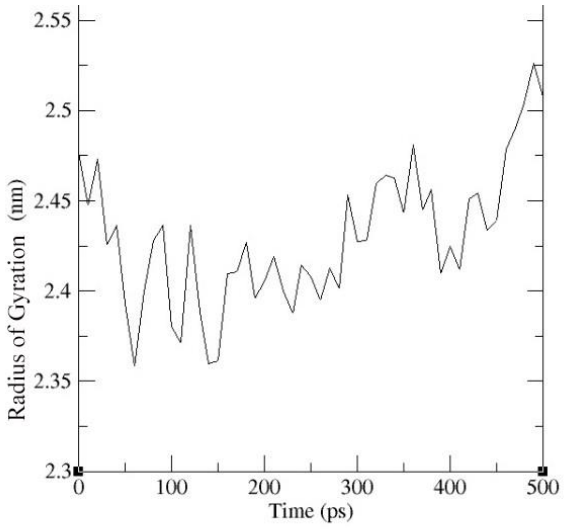

Fig 3.4 Graph of Radius of Gyration of Amylose vs Time

$R_{g,avg}$ of Amylose is 1.472 nm.

4. Future aspects and conclusion

- The equilibrated system of the hydrogel prepared can be used as an adsorbent when simulated with clay nanoparticles with the clay nanoparticles and heavy metals behaving as adsorbates.

- The surface of clay MMT can adsorb certain heavy metal particles on its surface.

5. Online References

1.https://onlinelibrary.wiley.com/doi/abs/10.1002/app.38052

2.https://www.sciencedirect.com/science/article/pii/S1385894714000904

3.https://link.springer.com/article/10.1023%2FA%3A1022308705231

4.https://www.sciencedirect.com/science/article/pii/S0308814606003074

5.https://www.sciencedirect.com/science/article/pii/S2090123213000969

6. Appendix

1. Pack using Packmol
    - Put the .pdb files of Amylose, Amylopectin, Sorbitol and water in the Packmol folder.
    - Prepare an input.inp file using the number of chains as:

```
# A mixture of Amylopectin, Amylose, Sorbitol and Water

tolerance 2.0
filetype – pdb
output mixture.pdb
structure Amylose.pdb
number 21
inside box 0. 0. 0. 230. 230. 230.
end structure

structure Amylopectine.pdb
number 10
inside box 0. 0. 0. 230. 230. 230.
end structure

structure sorbitol_e.pdb
number 1066
inside box 0. 0. 0. 230. 230. 230.
end structure

structure water.pdb
number 4
inside box 0. 0. 0. 230. 230. 230.
end structure
```

    - Start the packing process using the command:
      ./packmol < input.inp

   This will generate a mixture.pdb file.

2. To prepare the topology folder:
    - Create topology (.top,and .itp files) for individual single chains of molecules(amylose, amylopectin,sorbitol). Rename them with the names of respective molecules.

- Put the .gro and .top file of the packed ‘mixture.pdb’ file in the same folder.
- Next, edit the .top file with the number of chains which was used in packing.
- Do other necessary edits. (Our topology folder can be taken as reference)

3. Solvation
    - Command-

      gmx solvate -cp mixture_newbox.gro -cs spc216.gro -o mixture_solv.gro -p topol.top
4. Energy Minimization
    - Make a minim.mpd file by considering minimization process by Steepest Descent Minimization.
    - Command-

      gmx grompp -f minim.mdp -c mixture_solv.gro -p topol.top -o em.tpr -
      will assemble the binary input

      gmx mdrun -v -deffnm em
5. Equilibration
    - For NVT,after making nvt.mdp file
        - Commands-

          gmx grompp -f nvt.mdp -c em.gro -p topol.top -o nvt.tpr

          gmx mdrun -deffnm nvt

    - For NPT,after making npt.mdp file
        - Commands-

          gmx grompp -f npt.mdp -c em.gro -p topol.top -o nvt.tpr

          gmx mdrun -deffnm npt
6. To plot the graphs of temperature, pressure and density

    - Command –

      gmx energy -f npt.edr -o temperature.xvg
    - Gromacs will now prompt you to choose temperature. Choose the number and press enter twice.
    - The command “xmgrace temperature.xvg” will plot the graph of temperature vs time.
    - Similarly other graphs can also be plotted.

7. The radius of gyration of a protein is a measure of its compactness. If a protein is stably folded, it will likely maintain a relatively steady value of Rg. If a protein unfolds, its Rg will change over time.

   To find Radius of Gyration of single chain of molecules:

Generally, gmx gyrate, polystat, msd like gromacs commands do not prompt to select chains, so we need to create an index(index.ndx) file to add extra groups.
Steps :

- Preparation of input.ndx file:
    - Command - gmx make_ndx -f npt.gro –o index.ndx
    - Now we select residue associated with the molecule we want to group.

  For Amylose, we select- AGI, AGM, and AGF.
  In the command line - nr(AGI)|nr(AGM)|nr(AGF). Press enter
- Similarly, for Amylopectin and Sorbitol. Press 'q' to save and exit.
  Note:The information about residues in a particular chain may be obtained from their respective .pdb or .itp files.

- Now, we can calculate Radius of gyration for individual chains:
    - Command for Amylose:
        - gmx polystat –s npt.tpr –f npt.trr –n index.ndx –o Amylose.xvg
- On prompt choose the group corresponding to Amylose.
  Now, to plot Rg vs time- xmgrace Amylose.xvg

  Similar analysis can be done for Amylopectin and Sorbitol also.

8. Calculation in Section 2.3:

Assume total weight of system as 'x' gram.

Then, Weight of TPS= 0.1'x' gm
Its density= 1.34 gm/cm^3
Its volume = (0.1x/1.34) cm^3
Weight of water= .9x gm
Its density= 1gm/cm^3
Its volume = 0.9x cm^3
So, total volume = 0.975x cm^3
Equating it to $12.17X10^{-18}$ cm^3 will give x.
=> Weight of TPS (x) = W_n= 0.1x=1.2478 X 10^{-18}g
Which gives W_n/W_i = 0.23

*In Cluster,

Folder for 15nm system is named as '15nmsys'

Folder for 23nm system is named as '23nmsys'

Correct topology folder for Akash sir's system of TPS is named as 'topology'