Solvent selection in membrane preparation from polyethylene terephthalate plastic waste: computational and experimental study

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Abstract

The selection of the solvent during the membrane preparation process significantly affects the characteristics of the resulting membrane. The large number of organic solvents available for dissolving polymers renders this experimental approach ineffective. A computational approach can select a solvent using the solvation energy value approach. In addition, no organic waste is generated from the computational approach, which is a distinct advantage. A computational approach using the DFT/B3LYP/def2-TZVP RIJCOSX method was used to optimize the structure of polyethylene terephthalate (PET). The PET for the experiment was obtained from the utilization of plastic bottle waste. In addition, a review of the thermodynamics, geometry, HOMO-LUMO orbitals, and vibrational frequencies was conducted to validate the PET molecule against the experimental results. A conductor-like polarizable continuum model was used to determine the best solvent for dissolving the PET plastic waste. The results demonstrated that the Fourier Transform Infra-Red and Fourier Transform Raman spectra obtained from computational calculations were not significantly different from the experimental results. Based on a thermodynamic approach, computationally the Gibbs free energy (−724.723), entropy (0.0428), and enthalpy (−724,723 Kjmol⁻¹) values of the PET dimer molecule are not much different from the experimental values (−601, 0.042, and −488 Kjmol⁻¹). The computational approach was successful in selecting solvents that can dissolve PET plastic bottle waste. Phenol solvent has the lowest solvation energy value (−101.879 Kjmol⁻¹) and the highest binding energy (2.4 Kjmol⁻¹) than other solvents. Computational and experimental results demonstrated that the phenol solvent was able to dissolve PET plastic bottle waste better than the other solvents.

1. Introduction

Polyethylene terephthalate (PET) is a polymer with an ester (−COO) functional group, a benzene ring, and an alkyl [1]. In everyday life, PET is frequently used for packaging food and drinks. PET plastic bottle trash has been increasing owing to the use of PET polymer, which is used at a rate of approximately 381.73 million tons per year, and this has a detrimental effect on the environment [2]. PET plastic bottle trash can be used as a membrane material because it can create thin films or layers, making it a potential solution (membranes). Additionally, this method can prevent the environmental contamination caused by the increasing volume of plastic bottle waste that cannot be degraded. Few studies have used PET plastic bottle waste as a membrane. Although PET has hydrophilic functional groups (−CO, −COO, and -O), it has the potential to produce high water flux in the membrane.

In the process of preparing the membrane, using an effective solvent for dissolving PET is crucial because it affects the properties of the final membrane, such as its hydrophilicity. The dissolution of PET was tested using
various solvents, including acetic acid, acetone, chloroform, dichloromethane, dimethylformamide, dimethyl sulfoxide, ethanol, ethyl acetate, formic acid, methanol, methyl acetate, tetrahydrofuran, water, n-butanol, acetonitrile, glycerol, and trifluoroacetic acid [3]. The proposed computational approach is suitable for selecting several solvents for dissolving PET because it can reduce costs, labor costs, raw materials, and toxic waste generated from the experiments [4]. Understanding molecular characteristics, such as bond lengths, bond angles, torsion angles, and other geometric parameters that cannot be explained experimentally is another application of computational chemistry. Several studies have frequently referred to the solvation energy value when describing the interactions between the solvent and solute molecules [5–9]. If the value of the solvation energy (Gibbs free energy) is negative, it indicates that the solvation process can occur or be spontaneous, which is thermodynamically desired. Because it is believed to be more accurate than other approaches, the quantum chemical density functional theory (DFT) technique is frequently used in molecular computations [6, 10–12].

The most often employed hybrid functional DFT for solvents implicitly offers higher accuracy than other functional hybrids such as B3LYP [10]. In Orca, it is recommended to employ basis sets and auxiliary base sets such as def2-TZVP RIJCOSX for computations such as single-point energies, optimizations, and frequencies [13]. Furthermore, it has been reported that the conductor-like polarizable continuum model (CPCM) solvation model is extremely accurate in reproducing the solvation process [14, 15]. Therefore, the PET structure was optimized and the frequency was determined using the DFT/B3LYP/def2-TZVP RIJCOSX method, and the CPCM solvation model was used to determine the best solvent for old PET plastic bottles based on the solvation energy value. The outcomes of the laboratory trials and the computations were compared. This study also provides an overview of thermodynamic characteristics, including electronic energy, enthalpy, entropy, and Gibbs free energy, in addition to geometric factors such as bond length, bond angle, and dipole moment. The HOMO and LUMO orbitals were also used to explain the changes in the electron density in PET molecules. To confirm that the PET molecule utilized in the computations did not deviate significantly from the PET molecule used in the experiment, FTIR and FT-Raman spectra were also examined. N-methyl-2-pyrrolidone (C5H9NO), dimethyl sulfoxide (CH3)2SO, toluene (C6H5CH3), ethanol (C2H5OH), phenol (C6H5OH), dimethylformamide (CH3)2NC(O)H, acetone (C3H6O), trichloroacetic acid (CCl3COOH), and water (H2O) were the solvents used in this study.

2. Experimental method

Recycling PET resin-made plastic bottles yielded PET. The solvents used to dissolve PET include N-methyl-2-pyrrolidone (C5H9NO), dimethyl sulfoxide (CH3)2SO, toluene (C6H5CH3), ethanol (C2H5OH), phenol (C6H5OH), dimethylformamide (CH3)2NC(O)H, acetone (C3H6O), and trichloroacetic acid (CCl3COOH), obtained from Merck, Germany, (99%), and water (H2O) obtained from local suppliers in Indonesia. Waste PET plastic bottles were carefully cleaned before drying for 30 min at 30°C in an oven. To make the dried plastic trash easier to dissolve, it was broken into pieces of approximately ±1 cm × 1 cm. Up to 2.5 grams of plastic garbage was weighed and placed in a Duran container with a solvent. The solvents used in this study were the same as those previously discussed. When homogenous, the dissolution process was conducted in the dark using a magnetic stirrer at a speed of 200 rpm and temperature of 100°C. The homogeneous membrane impression solution was stirred, allowed to stand to eliminate air bubbles, and subsequently poured onto a glass plate with tapered edges to control the thickness of the membrane. Thereafter, the sample was placed in a phase transformation bath that included ethanol and water in a 15:1 ratio.

Analysis of the functional groups of the PET membrane used Fourier Transform Infra-Red (FTIR, Shimadzu) in the wave number region of 400–4000 cm⁻¹. While the morphological analysis of the membrane used a scanning electron microscope (SEM, Zeis EVO MA10).

3. Computational methodology

Using Orca 4.0, DFT calculations were used to optimize the PET structure. The PET structure and nine solvents were optimized using the B3LYP technique and the base set def2-SVP. The characteristics of the PET molecule (monomer, dimer, trimer, and tetramer) are shown in table 1. The Avogadro software was used to view the properties of the solvent employed in the computational simulations (table 2). Gibbs free energy values and experimental findings were compared as part of the PET molecule validation procedure, which was used to ascertain the structure of the PET molecule before it was solvated. The optimized structure exhibited wavelength, bond angle, torsion angle, HOMO-LUMO, and polarity molecular characteristics. The improved PET structure also exhibited Raman and vibrational wavenumbers. A CPCM solvation model was used to determine the best PET solvent. Gibbs free energy, enthalpy, and entropy of solvation of PET molecules in various solvents were also reviewed to determine the best solvent.
4. Results and discussion

4.1. Selection of the PET molecular structure

The optimized PET molecular structure obtained using Orca 4.0 and the DFT/B3LYP/def2-SVP calculation technique is shown in Figure 1. The optimal PET molecular structure comprises monomers \((n = 1)\), dimers \((n = 2)\), trimers \((n = 3)\), and tetramers \((n = 4)\). Different energies are observed for the four molecules (Table 3).

The increase in optimization energy, enthalpy, entropy, and Gibbs energy increases with increasing monomer number \((n)\). This increase in energy is caused by an increase in the number of atoms and electrons when PET monomers are produced, which increases the required energy. In addition, the dipole moment increases as the number of monomers increase. The increase in the number of atomic groups with several electrons causes the value to increase (O groups). The difference between 'positive charge' and 'negative charge' in the PET molecule increases with the inclusion of the O atomic group. The increase in molecular polarity supports the growing dipole moment.

![Molecular structure of: (a) monomer, (b) dimer, (c) trimer, and (d) tetramer.](image)

**Table 1.** The molecular characteristics of PET.

| Parameters                     | Monomer | Dimer | Trimer | Tetramer |
|--------------------------------|---------|-------|--------|----------|
| Molecular Weight (g mol\(^{-1}\)) | 210.183 | 402.352 | 594.520 | 786.688  |
| Chemical Formula               | \(C_{\text{n0}}H_{\text{n1}}O_{\text{n2}}\) | \(C_{\text{n2}}H_{\text{n3}}O_{\text{n4}}\) | \(C_{\text{n3}}H_{\text{n4}}O_{\text{n5}}\) | \(C_{\text{n4}}H_{\text{n5}}O_{\text{n6}}\) |
| Estimated Dipole Moment (D)    | 2.324   | 2.319 | 2.429  | 2.343    |
| Number of Atoms                | 25      | 47    | 69     | 91       |
| Number of Bonds                | 25      | 48    | 71     | 94       |
| Number of electrons            | 110     | 210   | 310    | 410      |
| Number of Monomers             | 1       | 2     | 3      | 4        |

**Table 2.** Molecular characteristics of the solvents.

| Parameters                     | Water | Acetone | Ethanol | DMF | DMSO | Toluene | NMP | TCA | Phenol |
|--------------------------------|-------|---------|---------|-----|------|---------|-----|-----|--------|
| Molecular Weight (g mol\(^{-1}\)) | 18.015 | 58.079  | 46.068  | 73.094 | 78.133 | 99.131  | 163.387 | 94.111 |
| Chemical Formula               | \(H_2O\) | \(C_3H_6O\) | \(C_2H_2O\) | \(C_2H_2NO\) | \((CH_2)_3SO\) | \(C_2H_3CH_3\) | \(C_2H_2NO\) | \(C_2HCl_3O_2\) | \(C_6H_6O\) |
| Number of Atoms                | 3      | 10      | 9       | 12    | 10    | 15      | 16   | 8   | 13     |
| Number of Bonds                | 2      | 9       | 8       | 11    | 9     | 15      | 16   | 7   | 13     |
| Dielectric constant (\(\varepsilon\)) | 80.4   | 20.7    | 24.3    | 38.3  | 47.2  | 2.4     | 32.16 | 8.55 | 15     |
| Refractive index               | 1.33   | 1.359   | 1.361   | 1.430 | 1.479 | 1.497   | 2.15 | 1.28 | 2.37   |

4. Results and discussion

4.1. Selection of the PET molecular structure

The optimized PET molecular structure obtained using Orca 4.0 and the DFT/B3LYP/def2-SVP calculation technique is shown in Figure 1. The optimal PET molecular structure comprises monomers \((n = 1)\), dimers \((n = 2)\), trimers \((n = 3)\), and tetramers \((n = 4)\). Different energies are observed for the four molecules (Table 3). The obtained energy value is the energy per unit. The increase in optimization energy, enthalpy, entropy, and Gibbs energy increases with increasing monomer number \((n)\). This increase in energy is caused by an increase in the number of atoms and electrons when PET monomers are produced, which increases the required energy. In addition, the dipole moment increases as the number of monomers increase. The increase in the number of atomic groups with several electrons causes the value to increase (O groups). The difference between 'positive charge' and 'negative charge' in the PET molecule increases with the inclusion of the O atomic group. The increase in molecular polarity supports the growing dipole moment.
The structure of the PET molecule to be solvated is selected by considering thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy. The decision is made using a thermodynamic energy value that deviates the least from the experimental results. Based on the computational and experimental results, the value of the thermodynamic energy differs slightly. This difference is due to the use of the gas phase in the computation and the solid phase in the experiment. This process is exothermic because the enthalpy is negative. While the enthalpy value from the computational results is the overall enthalpy, the enthalpy value from the experimental data is the enthalpy of production of the PET molecule (one PET molecule). Therefore, it is impossible to use the enthalpy value as a guide for selecting PET molecules. The reaction is considered spontaneous if the entropy values are positive and the Gibbs values are negative. Entropy, which is low and positive, indicates that there is little chaos in the PET molecule. The computational results demonstrated that dimers deviate slightly from the experimental data in terms of entropy and Gibbs free energy when compared to monomers, trimers, and tetramers (figures 2 and 3). To represent the qualities and traits of PET in the laboratory, dimers were used in the subsequent solvation process.

4.2. Molecular geometry of PET

The structure of the PET molecule to be solvated is selected by considering thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy. The decision is made using a thermodynamic energy value that deviates the least from the experimental results. Based on the computational and experimental results, the value of the thermodynamic energy differs slightly. This difference is due to the use of the gas phase in the computation and the solid phase in the experiment. This process is exothermic because the enthalpy is negative. While the enthalpy value from the computational results is the overall enthalpy, the enthalpy value from the experimental data is the enthalpy of production of the PET molecule (one PET molecule). Therefore, it is impossible to use the enthalpy value as a guide for selecting PET molecules. The reaction is considered spontaneous if the entropy values are positive and the Gibbs values are negative. Entropy, which is low and positive, indicates that there is little chaos in the PET molecule. The computational results demonstrated that dimers deviate slightly from the experimental data in terms of entropy and Gibbs free energy when compared to monomers, trimers, and tetramers (figures 2 and 3). To represent the qualities and traits of PET in the laboratory, dimers were used in the subsequent solvation process.

4.2. Molecular geometry of PET

The molecular structure of PET has a functional group of one aromatic ring, two carboxyl groups (-COO-), and one hydroxyl group (-OH) (figure 4). PET is a polyester polymer formed from terephthalic acid and ethylene glycol [17]. The carboxyl and hydroxyl groups in PET endows it with polar properties. This polar nature causes PET to dissolve in polar solvents. The bond length and bond angle parameters are listed in table 4. There was a slight variance between the experimental and computational results due to the gas phase used in the computation and the solid phase used in the experiment. The C–C bond lengths in the aromatic ring were 1.398 and 1.386 Å (computational) and 1.396 and 1.382 Å (experimental). The carbon atom attached to the carboxyl...
4.3. HOMO-LUMO analysis

HOMO-LUMO energy data is frequently employed to understand different chemical interactions [19]. Using the distribution of molecular orbitals around the atom, this information can be used to determine the reactivity...
and active sites of a molecule. Figure 5 shows the HOMO-LUMO orbitals calculated using the DFT/B3LYP/def2-SVP technique. The HOMO and LUMO orbitals of the PET molecule exhibit conjugation and delocalization of the positive and negative charges around the atom in blue and red, respectively. The COO-ester functional group was observed to have a negative charge at its center, whereas the CH2-CH2 group was the focal point of the positive charge. The ethyl group of the PET molecule did not exhibit charge delocalization in the HOMO or LUMO orbitals. Energy calculations for the HOMO-LUMO orbitals were also performed in this study. The energies of the HOMO and LUMO orbitals were $-7.549$ and $-2.271$ eV, respectively. The difference between the energies of the HOMO and LUMO was 5.28 eV. The energies of the HOMO-1 and LUMO+1 orbitals were $-7.772$ and $-1.012$ eV, respectively. The difference in value between the energies of HOMO-1 and LUMO+1 was 6.76 eV. The energies of the HOMO-2 and LUMO+2 orbitals were $-7.823$ and 0.024 eV, respectively. The difference between the energies of HOMO-2 and LUMO+2 was 7.85 eV. An increase in the energy difference is often associated with the electronic transition of a molecule [19].

4.4. FT-IR and FT-raman analysis

A comparison of the FTIR PET spectra produced experimentally [20, 21] and computationally is shown in figure 6(a). The functional groups observed in the PET molecules were examined using FTIR. The wavenumber

| Bond | Exp. | Comp. | Bond | Exp. | Comp. |
|------|------|-------|------|------|-------|
| O1-H16 | — | 0.965 | H16-O1-C2 | — | 111.34 |
| O1-C2 | — | 1.354 | O1-C2-O4 | — | 119.72 |
| O1-C2 | — | 1.201 | O1-C2-C4 | — | 122.87 |
| C2-C4 | — | 1.502 | O1-C2-C4 | — | 117.41 |
| C2-C4 | 1.3961 | 1.398 | C2-C4-C6 | 120.28 | 124.05 |
| C2-C6 | 1.084 | 1.084 | C2-C4-C6 | 118.54 | 116.81 |
| C2-C6 | 1.3825 | 1.386 | C2-C4-C6 | — | 119.12 |
| C2-C6 | — | 1.082 | C2-C6-C8 | — | 118.30 |
| C2-C8 | 1.3913 | 1.394 | C2-C6-C8 | — | 120.58 |
| C2-C8 | 1.3962 | 1.397 | C2-C6-C8 | — | 121.12 |
| H2-C2-C6 | — | 120.09 |
| C2-C6 | 1.3824 | 1.384 | H2-C2-C6 | — | 119.75 |
| C2-C6 | 1.3908 | 1.396 | H2-C2-C6 | — | 120.15 |
| C3-H17 | — | 1.081 | C10-C2-C6 | 118.64 | 118.00 |
| C3-C12 | 1.4883 | 1.493 | C6-C2-C8 | — | 119.62 |
| C11-O12 | 1.2324 | 1.207 | H17-C2-C8 | — | 121.37 |
| C11-O11 | 1.3406 | 1.346 | H17-C2-C8 | — | 121.06 |
| O11-C13 | 1.3686 | 1.440 | H17-C2-C8 | — | 117.98 |
| C13-H21 | — | 1.090 | H17-C2-C8 | — | 121.54 |
| C13-C14 | 1.5076 | 1.521 | H17-C2-C8 | — | 120.45 |
| C13-H22 | — | 1.096 | H17-C2-C8 | — | 120.45 |
| C13-C14 | 1.3690 | 1.419 | H17-C2-C8 | — | 120.45 |
| O13-H13 | — | 0.963 | C10-C10-C7 | 111.04 | 112.09 |
| C10-O11-C13 | 112.85 | 117.07 |
| C10-O11-C13 | 112.85 | 117.07 |
| H16-O1-C2-O3 | 171.2 | H31-C31-C14 | — | 111.08 |
| H32-O32-C14-H24 | 53.17 | H31-C31-O11 | — | 109.97 |
| H17-C17-O17-C10 | 65.29 | H21-C21-C22 | — | 108.15 |
| C2-C2-C6-C17 | 178.57 | O1-C1-C14 | 103.45 | 106.69 |
| C2-C2-C10-C6 | 179.66 | H2-C2-C14 | — | 111.88 |
| C2-C2-C6-C10 | 1.49 | H2-C2-C14 | — | 109.26 |
| O12-C10-C11-C10 | 179.97 | H2-C2-C14 | — | 106.50 |
| H19-C4-C5-H17 | 179.58 | H2-C2-C14 | — | 109.68 |
| C4-C4-C5-O1 | 159.31 | H2-C2-C14 | — | 107.52 |
| C4-C4-C5-O1 | 160.98 | C1-C10-O10 | 103.36 | 111.08 |
| H19-C5-C6-C7 | 62.42 | H4-C4-O13 | — | 111.82 |
| H23-C21-C13-O11 | 57.40 | H4-C4-O13 | — | 110.10 |
| H24-C14-C13-O11 | 59.44 | C14-O11-H23 | — | 109.28 |

Table 4. Geometric parameters of bond length (Å) and bond angle (°).

Bond length $R^2 = 0.9976$; bond angle $R^2 = 0.9863$

* as reported in a previous study [18]
used to observe the FTIR spectra was in the range of 4000–400 cm$^{-1}$. In the wavenumber range of 3100–3000 cm$^{-1}$ (computing), and 3055–2970 cm$^{-1}$ (experimental), C–H phenyl ring stretching and C–H ethyl stretching, respectively, were detected. The existence of C=O and C–O stretching functional groups was demonstrated by the absorption areas of 1725 and 1157 cm$^{-1}$ (experimental) and 1760 and 1260 cm$^{-1}$ (computational). The absorption areas for CH$_2$ and C–H blending were 1430 and 623 cm$^{-1}$ (experimental) and 1431 and 715 cm$^{-1}$ (computational), respectively. The differences between the gas phase employed in the computation and the solid phase used in the experiment accounted for the slight discrepancy in the absorption peak levels between the
experimental and computational results in the FTIR spectra. The results of the Raman spectra obtained using experimental and computational Raman shift values. In the experimental region between 795.2, 823.4, and 1058.8 cm$^{-1}$ and 868.2, 1100, and 1200 cm$^{-1}$, the ester and ester bending functional groups were observed (computing). The presence of CH$_2$ bending was indicated by the areas of 1234.1 cm$^{-1}$ (experimental) and 1351.7 cm$^{-1}$ (computational). High-intensity absorption regions corresponding to the C=O and C–O groups were observed at 1556.4 and 1672.9 cm$^{-1}$ (experimental), and 1688.2 and 1877.6 cm$^{-1}$ (computing). In the regions of 2945.8 and 3077.6 cm$^{-1}$ (experimental) and 3048.2 and 3224.2 cm$^{-1}$ (computational), aromatic CH–O and C–H were observed. The FTIR and FT-Raman data demonstrated that the PET molecule may computationally reflect the experimental results.

4.5. Selection of the best solvent

Organic solvents are frequently used to dissolve the polymers. The features of the resulting membranes in membrane applications are significantly influenced by the capacity of the organic solvents to dissolve the polymers. Prior to the phase inversion process, the solvent was added during the production of the dope solution. A good solvent for the PET plastic bottle trash was selected using computational and experimental analyses of the nine solvents. A computational strategy based on the solvation energy value produced [14, 24]. The experimental strategy was based on the ability of the nine solvents to dissolve PET plastic bottle waste in a laboratory setting. The outcomes from the two studies were compared. In this study, the varying characteristics and spectra of the PET molecules were examined.

The dipole moment increased from pure PET (3.30 Debye) to more than 3.98 Debye, indicating that the computational process of dissolving PET molecules in the nine solvents increased the polarity (table 5). The fact that the solvent utilized is a polar solvent causes the dipole moment to increase in value. Each solvent has nucleophilic functional groups, including C=O, O–H, C–N, S=O, COOH, and C–Cl, which alter the electron density around the PET molecule. This alteration increases the difference between positive and negative charges, producing a disproportionately large dipole moment. Furthermore, thermodynamic quantities, such as enthalpy, entropy, and Gibbs free energy, indicate the stability of the solvation system. The solvation system released heat, as indicated by the negative enthalpy value (exothermic). The entropy and Gibbs free energy of the solvation system indicate that the process is spontaneous, or it is capable of occurring. A positive entropy value and a negative Gibbs free energy indicate a spontaneous process. The Gibbs free energy, which is produced by the thermodynamic difference between enthalpy and entropy at a particular temperature, differs slightly from enthalpy because the entropy value is low.

When PET is dissolved, the interaction between solvent molecules is referred to as the solvation energy. The solvation mechanism passes through a number of steps (figure 7). The first step is the creation of a cavity or empty space in the solvent such that the solute can fit inside. The first process will have an impact on the entropy and enthalpy values of the system because the interactions of the solvent molecules are broken down to generate cavities. A high enthalpy value for the development of cavities results from strong interactions between the solvents. The cavity created by the solvent was filled with PET as the solute. The entropy value of the solvent system increased as a result of the establishment of PET. The entropy value of PET increased from $-0.057$ Hartree (before solvation) to $-0.0772$ to $-0.0789$ Hartree (after solvation) (tables 3 and 5).

A reduced or negative solvation energy value indicates that the solvent can thermodynamically dissolve PET [5, 7]. It was demonstrated mathematically that the Gibbs free energy of the system drops because the change in enthalpy is less than the change in entropy multiplied by the absolute temperature in Kelvin. All PET solvation energy values in the nine solvents were negative, according to the computational results. The phenol solvent exhibits a lower solvation energy than the other eight solvents, according to the solvation energy measurements. In comparison to other solvents, phenol, which is acidic, has been demonstrated in experiments to be able to dissolve PET plastic bottle trash. Theoretically, TCA solvent, which is nearly identical to phenol in terms of solvation energy, can also dissolve phenol. Experiments revealed that PET plastic bottle waste was not dissolved in TCA solvent. TCA is a solvent that is not considered ecologically friendly; therefore, its use in the membrane production procedure will limit the future utility of the membrane. However, because TCA is more expensive and environmentally harmful than phenol, researchers have rarely employed it. The inability of toluene, DMF, DMSO, water, acetone, ethanol, and NMP to dissolve PET plastic bottle waste has been experimentally proved. Figure 8 shows the method by which PET molecules dissolve in a phenol solvent. We attempted to employ a combination of the four substances based on solvation energy data, which indicated slight variance between phenol, TCA, DMF, and DMSO. The results demonstrated that the phenol/TCA, phenol/DMF, and phenol/
Table 5. Solvation of PET in various solvents.

| Parameters                  | Air       | Ethanol   | Aseton    | NMP       | Phenol    | DMF       | DMSO      | TCA       | Toluena   |
|-----------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Momen Dipole (Debye)        | 3.51      | 3.36      | 3.35      | 3.38      | 3.47      | 3.98      | 3.45      | 3.47      | 3.18      |
| Energi bebas Gibbs (Hartree) | −1449.551 | −1449.557 | −1449.560 | −1449.872 | −1449.570 | −1449.569 | −1449.569 | −1449.569 | −1449.569 |
| Entropy (Hartree)           | 0.0798    | 0.0788    | 0.0772    | 0.0778    | 0.0781    | 0.0783    | 0.0780    | 0.0780    | 0.0782    |
| Entalphi (Hartree)          | −1449.472 | −1449.454 | −1449.433 | −1449.565 | −1449.492 | −1449.491 | −1449.491 | −1449.492 | −1449.491 |
| Solvation Energy (Hartree)  | −0.0202   | −0.0210   | −0.0199   | −0.033    | −0.0388   | −0.0378   | −0.0376   | −0.0384   | −0.0349   |
| Solvation Energy (KJ mol$^{-1}$) | −53.136   | −55.225   | −52.124   | −87.722   | −101.879  | −99.383   | −98.817   | −100.937  | −91.563   |
| Binding Energy (KJ mol$^{-1}$) | 1.4       | 1.4       | 1.5       | 1.8       | 2.4       | 1.8       | 1.9       | 2.3       | 2.0       |
| Eksperiment                 | not dissolved | not dissolved | not dissolved | not dissolved | Dissolved | not dissolved | not dissolved | not dissolved | not dissolved |
DMSO solvent mixes did not dissolve the PET plastic bottle waste. The scheme for dissolving a PET-based plastic bottle in phenol solvent to form a membrane is shown in figure 9.

Figure 10 shows a comparison of the PET spectra before and after solvation in the nine solvents. The absorbance intensities of PET molecules vary before and after the solvation process. It was observed that the strength of the absorption peaks of the C=O and C–O ester stretching groups was greater than that of the pure
PET. Following the solvation process in the nine solvents, the intensity increased as a result of an increase in the dipole moment of the PET molecule (table 5). The differential electronegativity of the PET molecule may be increased by the nine solvents utilized because they were all polar solvents. Additionally, following the solvation process, the wavenumber value shifts in favor of a lower value. This change shows that the PET molecule requires more energy to vibrate because of the solvation process. When solvating polar solvents, the electron density increases, which is supported by an increase in the dipole moment, leading to a higher energy requirement.

5. Conclusions

The solvents that may effectively dissolve PET plastic bottle trash were selected using a computational methodology that makes use of the DFT/B3LYP/def2-TZVP RIJCOSX technology and the CPCM. The computational approach shows that the Gibbs free energy (−724,723), entropy (0.0428), and enthalpy (−724,723 KJmol$^{-1}$) values of the PET dimer molecule are not much different from the experimental values (−601, 0.04, and −488 KJmol$^{-1}$). The computational approach was successful in selecting solvents that can dissolve PET plastic bottle waste. Phenol solvent has the lowest solvation energy value (−101.879 KJmol$^{-1}$) and the highest binding energy (2.4 KJmol$^{-1}$) than other solvents.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Figure 10. Effect of the solvent on the FTIR spectra of PET.
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