Solvent and non-solvent selection for the chemical recycling of waste Polyethylene (PE) and Polypropylene (PP) metallized film packaging materials

Regino C. Gorre Jr.\textsuperscript{1,a} and Terence P. Tumolva\textsuperscript{1,b}

\textsuperscript{1} Green Materials Laboratory, Department of Chemical Engineering, University of the Philippines, Diliman, Quezon City 1101, Philippines.

E-mail: \textsuperscript{a} reginogorrejr1990@gmail.com, \textsuperscript{b} tptumolva@up.edu.ph

Abstract. A solvent and non-solvent selection method for the chemical recycling through selective dissolution and precipitation of multi-component waste metallized film wrapper is studied to recover Polyethylene (PE), Polypropylene (PP), and the metal film separately. Pre-selection of solvent for dissolution and non-solvent for precipitation is based on the similarity and compatibility of polymer and solvent molecules measured in terms of solubility parameter and calculated using group contribution approach through Hoftyzer and Van Krevelen method. Toxicity, cost, and availability of the solvent are also considered on the selection. A Hansen sphere model is developed for the prediction of polymer solubility in which \textit{p}-cymene, a low-cost and naturally derived solvent is chosen as solvent and acetone as non-solvent. PE was first recovered through dissolution at a given temperature, followed by precipitation. PP which remained undissolved together with the metal film was extracted through the same technique but with different dissolution temperature. FTIR spectra of the recovered polymers showed similarity compared to virgin PE and PP films. The melting point of the recovered PE and PP using \textit{p}-cymene determined in the DSC curves were 107.37 °C and 164.55 °C, respectively. Furthermore, the simplicity of the process, high recovery yield obtained, and the application of \textit{p}-cymene would make the recycling economical and environment-friendly.

Keywords: Solubility parameter, polymer dissolution, chemical recycling, PE, PP

1. Introduction

Plastic based packaging films are usually composed of multilayer combination of materials like metallized film laminate of polymer film and thin metal such as aluminum. Each component has different functions attributed to their physical properties like moisture barrier and gas permeability. Due to its multi-component layering, these types of wastes are difficult to recycle and methods of an efficient recycling are of great interest. Popular methods employed mechanical recycling through melt extrusion which demands more energy with lesser valuable product since for a plastic recyclates to be competitive in the market, it must possess properties akin to a virgin material [1]. These wastes accumulate in our landfills and end up polluting our oceans.
In 2010, the Philippines is ranked as the 3rd contributor of plastic pollution in the ocean, behind China and Indonesia, producing 1.88 MMT/year of mismanaged plastic waste [2].

One method of recycling thermoplastics such as PE and PP films is through dissolution and precipitation in a solvent and non-solvent system. Polymer dissolution is based on the concept of solubility parameter wherein materials with similar or same solubility parameter will tend to be soluble to each other [3,4].

Nauman et al. [5], showed that xylene may be an effective solvent for recycling of plastics using selective dissolution in a mixed waste stream composed of different commingled thermoplastics at different temperatures. Poulakis and Papaspyrides [6] studied the recycling of PP pipes dissolved in xylene up to the level of 0.15 kg/L at 135 °C and was precipitated using acetone. Further studies on the recycling of polyolefins were conducted by Achillas et al. [1] using dissolution/precipitation technique and pyrolysis. Toluene and xylene were used as solvents with boiling point of 110 °C and 140 °C respectively. In another study by Hadi et al. [7], recycling of polyolefins was examined using dissolution/precipitation method with mesitylene and petroleum ether as solvents and n-hexane as non-solvent. Although there are few studies applying polymer dissolution to plastic recycling, commercialization of this method is not widely implemented because of the following factors such as: previous studies used solvents which are toxic, expensive, and not locally available which are not environment-friendly, unsafe, and economical in terms of plastic recycling.

The selection of environment-friendly and low-cost solvents for an efficient recycling process that could produce higher recovery rate and quality recycled product is the subject of this research. In this study, the dissolution and precipitation technique are employed for the recycling of waste PE and PP metallized film. Pre-selection of solvents are based on the following criteria: efficiency, toxicity, and cost. Efficient solvent and non-solvent used to dissolve and precipitate the polymer are pre-selected through solubility parameter concept of Hansen solubility parameters calculated using group contribution approach by Hoftyzer and Van Krevelen [8]. The polymer solubility is predicted through Hansen sphere model [9]. Minimum dissolution temperature was first determined and the characterization of the precipitated polymers is carried out through ATR-FTIR spectroscopy and differential scanning calorimetry (DSC).

2. Material and Methods

2.1. Materials
13 um- thickness PE film, 20 um PP film (set as virgin materials) and waste metallized snack food wrapper were used in this study. The solvents used were cyclohexane, p-cymene, and acetone which were reagent grade purities and were purchased from Sigma Aldrich.

2.2. Solvent and non-solvent selection
Solvent/non-solvent system used were chosen based on the similarities of their solubility parameters with the polymer PE and PP. Group contribution approach by Hoftyzer and Van Krevelen was employed to calculate the Hansen solubility parameters of the solvents and polymers. A Hansen solubility sphere model is developed to predict the polymer solubility. Toxicity and cost were also evaluated in the selection process.

2.3. Solubility determination at different temperatures
Experiments were conducted at different temperatures to determine the minimum temperature at which complete dissolution would take place.

2.4. Sample preparation
Waste metallized wrapper samples are clean, cut into pieces and placed together with 150 mL of cyclohexane which is used as a paint-stripping solvent in a 250-mL enclosed stirred vessel. The paint-stripped wrapper is being filtered, recovered, and dried.
2.5. Dissolution and precipitation method

Paint-stripped wrapper samples were placed with p-cymene in a 250-mL enclosed stirred vessel equipped with a thermometer. The temperature was maintained and controlled at 95 °C to dissolve the PE in the sample. A non-solvent was added to the solution to precipitate the PE. The extracted polymer is filtered and dried in an oven. The undissolved solids containing the polymer PP and metal film is washed by acetone and dissolved in a 250-mL enclosed stirred vessel. The temperature was maintained at 120 °C to dissolve PP in the sample and precipitated through addition of a non-solvent. The extracted polymer is filtered and dried in an oven.

2.6 Characterization. ATR – FTIR spectrometer was used to characterize the chemical structure of the recovered and virgin polymers. The melting point temperatures and percent crystallinity are determined using DSC (TA DSC Q-20).

3. Results and Discussion

3.1 Solvent selection calculation

The Hoftyzer-Van Krevelen method could be used to theoretically predict the three solubility parameter components (Hansen solubility parameters) of PE and PP with different solvents through the group contribution approach using the three equations below [8]:

\[
\delta_D = \frac{\sum F_{Di}}{V_m}, F_{Di} = \text{group contribution to dispersion component of molar attraction} \tag{1}
\]

\[
\delta_P = \frac{\sum F_{Pi}}{V_m}, F_{Pi} = \text{group contribution to polar component of molar attraction} \tag{2}
\]

\[
\delta_H = \frac{\sum E_{Hi}}{V_m}, E_{Hi} = \text{group contribution to Hydrogen bonding of molar attraction} \tag{3}
\]

The Hansen solubility parameters of solvents and non-solvent chosen to dissolve and precipitate PE and PP are listed in Table 1.

| Substance         | MW [g/mol] | Density [g/cm³] | V_m [cm³/mol] | Group Contribution | F_D | F_P | F_H | δ_D | δ_P | δ_H |
|-------------------|------------|-----------------|---------------|--------------------|-----|-----|-----|-----|-----|-----|
| PE                | 28.10      | 0.93            | 30.38         | -CH₂ -             | 540 | 0   | 0   | 17.78| 0   | 0   |
| PP                | 42.10      | 0.90            | 46.67         | -CH₃               | 420 | 0   | 0   | 16.50| 0   | 0   |
|                  |            |                 |               | -CH₂ -             | 270 | 0   | 0   |       |     |     |
|                  |            |                 |               | >CH₋₋₋₋             | 80  | 0   | 0   |       |     |     |
| p-Cymene          | 134.2      | 0.86            | 156.60        | -CH₂ -             | 1260| 0   | 0   | 16.67| 0.35| 0   |
|                  |            |                 |               | -CH₃               | 80  | 0   | 0   |       |     |     |
|                  |            |                 |               | >CH₋₋₋₋             | 1270| 110 | 0   |       |     |     |
| Mesitylene        | 120.2      | 0.86            | 139.11        | -CH₂ -             | 1260| 0   | 0   | 18.19| 0   | 0   |
|                  |            |                 |               | -CH₃               | 80  | 0   | 0   |       |     |     |
|                  |            |                 |               | >CH₋₋₋₋             | 1270| 110 | 0   |       |     |     |
| Acetone           | 58.08      | 0.78            | 74.08         | -CH₂ -             | 840 | 0   | 0   | 15.25| 2.60| 5.20|
|                  |            |                 |               | -CO                | 290 | 770 | 2000|       |     |     |

The three Hansen parameters δ_D, δ_P, and δ_H can be represented as the coordinate of a point in the sphere model. A threshold value of 5 MPa^{1/2} on the solubility region of the polymer in the sphere is employed as the interaction radius, R_0. Solvents within the polymer solubility sphere will theoretically dissolve the polymer as shown in Figure 1 and 2 [8, 10].

Table 1. Calculated values of Hansen solubility parameters using Hoftyzer – Van Krevelen Method.
Figure 1. Hansen solubility parameter sphere model of PE.

Figure 2. Hansen solubility parameter sphere model of PP.

From Figure 1 and 2, cyclohexane, mesitylene, and \( p \)-cymene would likely dissolve PE and PP. Acetone, which is at the outside of the polymer’s interaction radius, could be used as a non-solvent.

**Table 2. Solvent and Non-solvent Toxicity and Cost Assessment.**

| Solvents and Non-solvent | Toxicity/Background | Global Hazard System Pictogram | Price, [PHP/L] |
|--------------------------|---------------------|-------------------------------|---------------|
| \( p \)-Cymene           | Naturally occurring compound from plant extracts | ![GH502, GH507](image) | 3,511.35 |
| Cyclohexane              | Prolonged exposure could damage target organs | ![GH507, GH506, GH509](image) ![GH502](image) | 5,010.75 |
| Mesitylene               | Major urban volatile organic compound (VOC) | ![GH507, GH508, GH509](image) ![GH502](image) | 5,018.40 |
| Acetone                  | Volatile and flammable liquid | ![GH502, GH507](image) | 4,551.75 |

From Figure 1, Figure 2, and Table 2, the solvent and non-solvent selected with the following criteria: efficiency, toxicity, cost (based from Sigma Aldrich), and availability are \( p \)-cymene and acetone.

### 3.2 Effect of temperature on solubility

The experiment is carried out at temperature below the boiling point of \( p \)-cymene which is at 177 °C. As shown in Figures 3, 4 and 5, an increase in solubility of the polymers using the three solvents is observed as the temperature is increased. Furthermore, \( p \)-cymene completely dissolves PE and PP at 95 °C and 120 °C, respectively.
3.3 Dissolution and precipitation
As shown in Figure 6, 78.43% and 93.92% average recovery yield for extracted PE and PP were achieved. P-Cymene is an efficient solvent in the dissolution of PE and PP while acetone is found to be a good precipitating agent with 1:1 solvent to non-solvent volumetric ratio. PE is recovered in a blue-colored and grain-shaped polymer; PP had white grain shaped polymer; while the metal film is left undissolved as seen in Figure 7. The blue color in the appearance of the recovered polymer indicates that paint from the wrapper is not totally removed.

3.4 Characterization
In Figure 8 and 9, the FTIR spectra of the recovered polymer PE and PP showed identical results compared to the virgin PE film and PP film. These indicate that no significant changes occurred on the chemical structure after the dissolution and precipitation processes. The obtained DSC curves are used to compute the percent crystallinity and to determine the melting point temperature of each polymer [11-12]. As shown in Figure 10 and 11, melting point temperatures of the recovered PE and PP are
107.37 °C and 164.55 °C. As presented in Table 3, the obtained percent crystallinity of the recovered PE and PP are 34.03% and 55.07%, respectively.

**Figure 8.** FT-IR spectra of PE in wrapper, virgin PE film and recovered PE.

**Figure 9.** FT-IR spectra of PP in wrapper, virgin PP film and recovered PP.

**Figure 10.** DSC curves of recovered and virgin PE.

**Figure 11.** DSC curves of recovered and virgin PP.

**Table 3.** Thermal analysis data of the recovered and virgin polymers PE and PP.

| Polymer          | $\Delta H_f$ [J/g] | Melting point [°C] | Crystallinity [%] |
|------------------|--------------------|--------------------|-------------------|
| Virgin PE film   | 94.28              | 116.93             | 32.18             |
| Recovered PE     | 99.72              | 107.37             | 34.03             |
| Virgin PP film   | 107.60             | 164.43             | 51.98             |
| Recovered PP     | 114.00             | 164.55             | 55.07             |
4. Conclusions

The application of \( p \)-cymene, a low-cost solvent and a naturally occurring organic compound that constitutes the essential oils from plant extracts, as solvent for dissolution and acetone as non-solvent for precipitation, leads to successful recovery of PE and PP from the waste metallized plastic wrapper with average percent recovery yield of 78.43% and 93.92%, respectively. ATR-FTIR results identified the recovered polymers as PE and PP, and had similar IR spectra with respect to the virgin PE and PP films. Chemical structure after the recycling method was not significantly altered. DSC curves showed comparable melting point temperature and percent crystallinity of the recovered polymers to the virgin PE and PP films. The melting point of the recovered PE and PP using \( p \)-cymene determined in the DSC curves were 107.37 °C and 164.55 °C, respectively.

References

[1] Achilias D S, et al. 2007 Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP) Journal of Hazardous Materials, 149(3), 536–542.
[2] Jambeck J R, et al. 2015 Science, 347(6223):768-771.
[3] Hansen C M 2007 Hansen Solubility Parameters A User’s Handbook.
[4] Burke J 2013 Solubility Parameters: Theory and Application. 1-33.
[5] Nauman E and Lynch J 1994 United States Patent US 5,278,282.
[6] Poulakis J G and Papaspyrides C D 1997 Resources, Conservation and Recycling Vol. 20, No. 1, 31-41.
[7] Hadi, A J, Najmuldeen G F and bin Yosuf K 2013 Energy Education Science and Technology Part A: Energy Science and Research, 30.
[8] Van Krevelen D W and te Nijenhuis K 2009 Properties of Polymers 4th Ed.
[9] Miller-Chou B and Koenig J L 2003 Progress in Polymer Science (Oxford), 28(8), 1223–1270.
[10] Kitak T, et al. 2015 Determination of solubility parameters of ibuprofen and ibuprofen lysinate. Molecules, 20(12), 21549–21568.
[11] Blaine RL 2010 Determination of Polymer Crystallinity by DSC. Therm Anal.;1–3.
[12] Wunderlich B 1990 Thermal analysis. Academic Press, Inc., 337.

Acknowledgement

The authors would like to express gratitude and acknowledge the Engineering Research and Development for Technology (ERDT) Scholarship program by the Department of Science and Technology (DOST) of the Republic of the Philippines for the financial support and encouragement towards the completion of this research.