Dissolution Kinetics of Low-Density Polyethylene in D-Limonene/Xylene Solutions for the Chemical Recycling of Waste Plastic Laminates

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Abstract. The dissolution-precipitation method has been identified as a potentially viable solution to plastic waste recycling in the Philippines. In this study, the effect of solvent temperature and composition on the dissolution kinetics of low-density polyethylene (LDPE) in D-limonene/xylene were determined. Dissolution temperature was varied within 100°-120°C with solvent composition of 0-100 wt% D-limonene for both 2-layer and 3-layer laminates of LDPE and polyethylene terephthalate (PET). The data were fitted to the Korsmeyer-Peppas model and the kinetic parameters were determined. Based on the experimental data, it was observed that there is no definitive relation between the dissolution rate and temperature for all solvent composition except at pure xylene, where the behavior at 110°C and 120°C appeared to be identical. It was also observed that introducing even a small amount of D-limonene to the solvent solution significantly increases the rate of dissolution, with a 1:3 limonene-to-xylene ratio having a K value that is 0.075 higher than that of pure xylene. Dissolution in D-limonene was observed to best fit the Fickian model, while that in xylene generally followed the non-Fickian model. Lastly, the 2-layer laminates showed to follow anomalous transport, wherein solvent diffusion and disentanglement of chains have comparable rates.

Index Terms: plastic laminates, dissolution-kinetics, chemical recycling

I. INTRODUCTION

An estimated 164 million plastic sachets are used daily in the Philippines alone according to a 2019 report published by the Global Alliance for Incinerator Alternatives [1]. The country is often referred to as a "sachet economy" wherein consumer products packaged in single-use plastic sachets dominate the market due to the lower-cost and lower-volume nature of products in sachet packaging. As a result of poor general waste management, the lack of proper waste destinations [2], and the lack of proper enforcement, spent sachets often end up as pollutants in both land and water. Sachets, in particular, result in waste consisting of multiple non-biodegradable polymers used in its layered composition, including but not limited to: polyethylene terephthalate (PET), vacuum metallized PET (VMPET), low density polyethylene (LDPE), and polyurethane (PU). Contemporarily, majority of developed countries use methods such as incineration [3], gasification, pyrolysis, and reprocessing in the melt-phase to address the problem of plastic waste. These, however, are not feasible in the Philippines as they are considered complex, laborious, expensive, energy-intensive, or violative of local clean emission legislation [4] [5] [6].

One plastic waste reduction method which shows great feasibility in the Philippine context is the dissolution-repricipitation process. Dissolution-repricipitation involves the selective dissolution of a single polymer in a blend of multiple polymer types. Separating the insoluble polymers, the dissolved polymer can be repricipitated using a non-solvent. The polymer is then recovered and can be reprocessed to be used as near-virgin material. Furthermore, it can deal with a complex mixture of plastics, bypassing the complicated sorting process, and its product quality is already comparable with virgin polymers [7]. A study by Escasa, et al. [8] used D-limonene as a solvent and ethanol as the non-solvent for the chemical recycling of plastic laminates. Use of other solvents such as Xylene may also be investigated.

The main objective of the study is to determine the most suitable kinetic model and its model parameters that will describe the solvent dissolution behavior of LDPE in various D-limonene/xylene systems. The study will also investigate the effects of temperature, solvent composition, and laminate type on the system and its model parameters.

II. MATERIALS AND METHODS

The dissolution procedure was executed using 2.5 cm x 2.5 cm sheets of 2-layer laminate (PET/LDPE) and 3-layer laminate (PET/VMPET/LDPE) sachets in a 50 mL of solution constantly stirred at 180 rpm held at temperatures 100 °C, 110 °C, and 120 °C and concentrations of v/v% 0%, 25%, 50%, 75%, and 100% D-limonene and balance xylene. Per time interval, the sheet samples are removed from the solvent, dried, weighed, and returned to the solvent. Gravimetric measurements were continued until a constant mass was obtained. This was taken as the complete dissolution of the LDPE layer.

Figure 1. Photographs of the 2-layer laminate sample in different stages of dissolution: (a) pre-dissolution; (b) mid-dissolution; (c) post-dissolution.
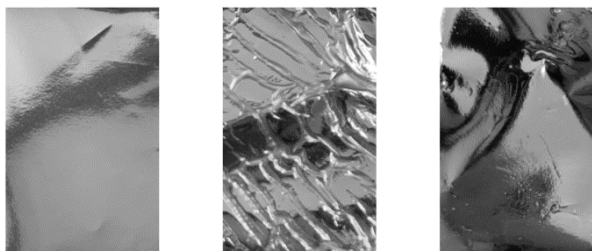
Figure 2. Photographs of the 3-layer laminate sample in different stages of dissolution: (a) pre-dissolution; (b) mid-dissolution; (c) post-dissolution.

III. RESULTS AND DISCUSSION

The fraction of PE dissolved vs. time data will be fitted into the Korsmeyers-Peppas model as shown in Equation 1. The results for a specific temperature, solvent composition, and laminate type are compared.

$$\frac{M_t}{M_\infty} = Kt^n$$

(1)

M_t and M_∞ correspond to the amount of polymer dissolved and the amount of polymer that can be dissolved, that is at equilibrium. The exponent n can vary depending on the geometry and mechanism. The geometry can either be planar (thin film), cylindrical, or spherical. As for the mechanism of dissolution, it can follow the Fickian and non-Fickian model. The Fickian model is governed by diffusion of the solvent and has an exponent n = 0.5. This generally occurs when the temperature of the environment is higher than the glass transition temperature of the polymer. When the polymer is in the rubbery state, the chains have a higher mobility. [9].

The non-Fickian model, on the other hand, can have an exponent of $0.5 < n \le 1$. The extreme case is having an exponent n = 1. This has the solvent diffusing much more rapidly and thus the behavior is governed by the swelling or disentanglement of polymer chains. If both the solvent diffusion and disentanglement of chains have comparable rates and both govern the dissolution process, it is of anomalous transport and can have varying values of n. A rare case is the Super Case II model wherein the exponent n > 1. Tension and breaking of the polymer occurs in the sorption process. [9]

The data after the swelling period were fitted into Equation 1 and the effect on the rate of dissolution of the different variables was observed. The rate of dissolution can be compared with the slope parameter K, wherein the higher the slope, the faster the rate of dissolution. The dissolution starts after the time of swelling, and by the end of dissolution, LDPE is approximately 98% dissolved. The K values of the graphs for each temperature, each solvent, and each laminate type are shown in Table 1, with the sample plots for 2-layer laminates at 100°C shown in Figure 3. The values of r^2 ranged between 0.96 and 0.99 for these data points in Table 1.
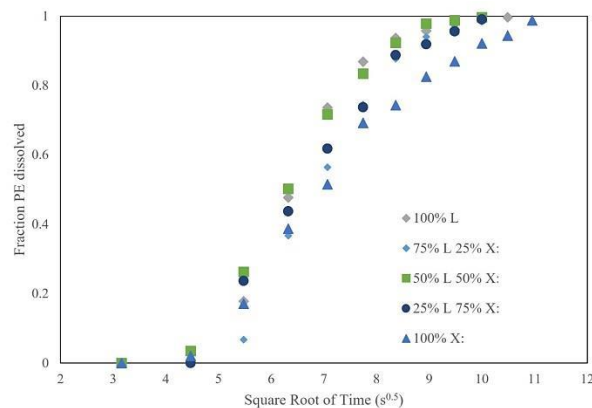
Figure 3. Fickian Power Law model graph for Two Layer Laminates at 100°C

For 2-layer laminates, for each type of solvent used, the rate of dissolution is almost the same for the temperatures used with a maximum deviation of 0.045, hence no temperature dependence can be seen except for 100% xylene. The rates of dissolution for 100% D-limonene are between 0.251-0.256, for 75% D-limonene 25% xylene are between 0.220-0.254, for 50% D-limonene 50% xylene are between 0.237-0.282, and for 25% D-limonene 75% xylene are between 0.207-0.227. For the tests using 100% xylene, it exhibited that higher temperatures increase rate of dissolution with 100°C being significantly lower at K = 0.152, however the slopes of the 110°C and 120°C, K = 0.230 and K = 0.238, are close to each other with only a difference of 0.008.

The trends observed with the slopes may show that using D-limonene as a solvent has already reached optimum rates beyond 100°C with respect to temperature, while

using xylene is still temperature dependent within the temperature range 100-120°C. It can be suggested that at 110°C, LDPE in xylene has already reached optimum rates and thus does not change its rate of dissolution significantly when the test is operated at a higher temperature of 120°C. Much like 2-layer laminates, the only increasing trend on the slope for 3 can be observed for 100% xylene, although insignificantly. It can also be observed that slope of the test with 120°C is higher than the slope of the tests with 100°C. The only increasing trend on the slope found for 3-layer laminate tests can be observed for 100% xylene. Deviations from Fickian behavior and failure to see some trends can be attributed to the difficulty of handling the samples. Some samples may roll, which can alter the geometry of the sample and leave much of the LDPE unexposed to the solvent.

may operate using the non-Fickian model. Some 2-layer laminates have better fit for anomalous transport ($0.5 < n < 1$) wherein solvent diffusion and disentanglement of chains have comparable rates, while those tests having 3-layer laminates may have as far as $n = 1$, or that solvent diffusion is very rapid and the dissolution process is governed by the disentanglement of polymer chains. One test, however, had $n = 0.607$, meaning it had anomalous transport using pure xylene at 110°C. LDPE in 3-layer laminates have more dense packing of polymeric chains and have higher molecular weights that its disentanglement can effectively hinder the rate of dissolution [9].

Table 1 : K values of Fickian Korsmeyers-Peppas model graphs

2-Layer Laminates					
	100% L	75% L 25% X	50% L 50% X	25% L 75% X	100% X
100 °C	0.254	0.254	0.237	0.227	0.152
110 °C	0.256	0.230	0.282	0.223	0.230
120 °C	0.251	0.220	0.254	0.207	0.238
3-Layer Laminates					
	100% L	75% L 25% X	50% L 50% X	25% L 75% X	100% X
100 °C	0.156	0.107	0.237	0.240	0.193
110 °C	0.308	0.271	0.222	0.213	0.210
120 °C	0.213	0.171	0.240	0.314	0.213

For 2-layer laminates, there is a decrease in slope as the xylene concentration increases at 100°C, while no trend is observable for 3-layer laminates at the same temperature. Introducing at least a small composition of limonene to the solvent solution at 100°C increases the rate of dissolution, with 25% limonene 75% xylene having a K value 0.075 higher than 100% xylene. No trend is observed at higher temperatures. Xylene dissolution is fastest beyond 100°C, and rates are comparable to limonene.

IV.   CONCLUSION

From fitting the data into the Korsmeyers-Peppas model operating under Fickian diffusion, the kinetic parameter K was obtained for each trial as a basis for rate of dissolution. The slope of Power law models were obtained and used to observe the temperature and solvent concentration dependence of the rate of dissolution of LDPE. For temperature dependence, a trend was only observed in 100% xylene and that increasing temperature

Table 2: K values of Fickian Korsmeyers-Peppas model graphs

2-Layer Laminates					
	100% L	75% L 25% X	50% L 50% X	25% L 75% X	100% X
100°C	0.500	0.500	0.500	0.500	0.500
110°C	0.500	0.500	0.731	0.500	0.804
120°C	0.500	0.591	0.500	0.500	0.500
3-Layer Laminates					
	100% L	75% L 25% X	50% L 50% X	25% L 75% X	100% X
100°C	0.500	0.500	1.000	0.500	0.500
110°C	0.500	0.500	1.000	0.500	0.607
120°C	0.500	0.500	0.500	1.000	0.500

The fit of the data were also optimized by obtaining the value of exponent n that results to the best coefficient of determination (r^2). Majority of the tests still operate on Fickian model ($n = 0.5$), with solvent diffusion as the main process governing the whole dissolution process. All the tests using pure D-limonene operate are best fitted using the Fickian model, while those with xylene

increases the rate of dissolution for both 2-layer and 3-layer laminates. For two layer laminates, there is a decrease in slope as the xylene concentration increases at 100°C, but has no effect at higher temperatures. Majority of the tests operate on Fickian model ($n = 0.5$), with solvent diffusion as the main process governing the whole dissolution process.

V. ACKNOWLEDGEMENT

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