Kanazawa Izumigaoka High School **02**

Recycling with Oranges: The Efficiency of Polystyrene Dissolution Using Limonene

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Abstract

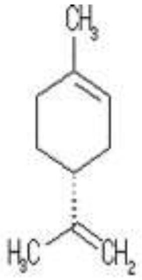
Today, about half of all polystyrene is wasted. We suggest recycling using limonene, a substance in oranges. Limonene dissolves polystyrene without emitting harmful gases, but at this moment, this way of recycling costs a lot. To know the best conditions for efficient dissolution, we measured time and dissolution speed at several temperatures. We succeeded in expressing the dissolution speed in a formula.

1. Introduction

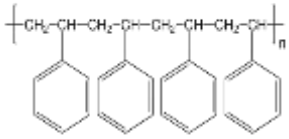
The juice from oranges bursts balloons. It's because limonene which is contained in the juice and has a similar chemical structure to polystyrene dissolves plastic(【figure1】【figure2】). We can get limonene from citrus-fruits such as oranges or grapefruits. We have come to think that we make use of limonene to recycle polystyrene. Now, our society utilizes as many as 40% of polystyrene as fuels and 50% of it as new materials. This means that we cannot reuse polystyrene fully. Moreover, this way of recycling emits carbon dioxide and has a bad influence on the environment. We also need a lot of energy to burn polystyrene. However, recycling using limonene can solve these problems. We can reuse all of the polystyrene and 99% of limonene as former forms, again and again. This way of recycling does not emit harmful gases or greenhouse effect gases because we do not have to burn polystyrene. However, we found a disadvantage. Recycling using limonene is expensive. Therefore, we made it our goal to find a method that is low cost and high efficiency when recycling polystyrene with limonene. For the first step, we research the relationship between dissolved mass of polystyrene and time due to changes in limonene temperature.

▼ information of limonene

- monocyclic monoterpene
- a chemical formula $C_{10}H_{16}$
- molecular weight 136.23
- density 0.8411g/㎤
- boiling point 449K(176℃)
- flash point 323K(50℃)



▲【figure1】 the structure of limonene



▲【figure2】the structure of polystyrene

2. Current method of recycling polystyrene with limonene

[1] Dissolve polystyrene in limonene solution.

[2] Heat the solution to remove limonene and recover polystyrene resin.
（Evaporated limonene will be reused after cooling.）

[3] Heat beaded polystyrene mixed with butane to re-effervescent.

3. Preceding studies

Sony Corporation developed a recycling method using limonene. In 2001, Eco Life Tosa Co., Ltd. carried out trial exam in Kochi Prefecture. However, as mentioned above, this method is costly. The cost can be suppressed to some extent by increasing the amount of polystyrene handled. Therefore, we wondered if it would be possible to reduce costs by increasing the efficiency of the polystyrene dissolving process.

4. Experiment1

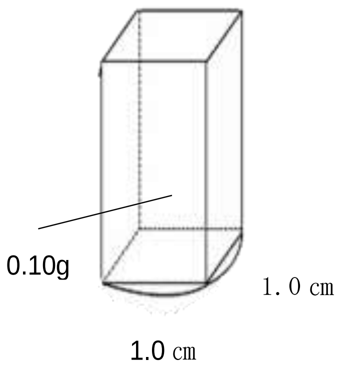
[1] Prepare a lot of polystyrene poles. Each pole is 0.10g and the base area is 1.0 ㎠. (【figure3】)

[2] Prepare 60ml of limonene in a 100ml beaker.

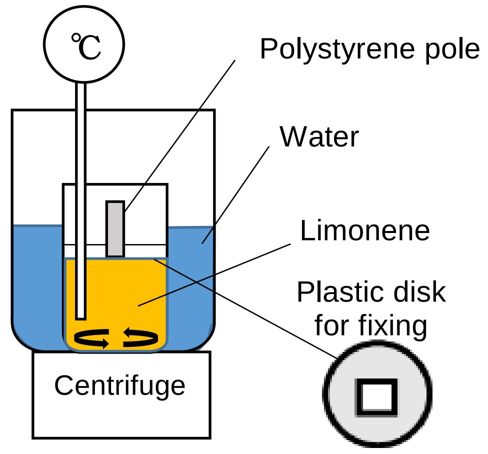
[3] Put one polystyrene pole into the beaker, and after the first one is dissolved, add the next one.

Note: While the pole is being dissolved, we used a centrifuge in the beaker of limonene to equalize the concentration in the solution.
Note: We fixed the polystyrene pole into the hole of a plastic disk, to make sure that area of the polystyrene pole exposed to the surface of limonene was always 1.0 ㎠(【figure4】).

We conducted this experiment under the following six temperatures, 4℃, 10℃, 20℃, 30℃, 40℃, 50℃. To keep each temperature constant, we put the beaker of the limonene into a larger beaker filled with ice or hot water to control the temperature.



▲【figure3】 polystyrene pole



▲【figure4】 experiment1

5. Hypothesis

$$\frac{dC}{dt} = \frac{DS}{V\delta}(Cs - C) \cdots (*)$$

$$D = \frac{R}{6\pi r\eta N} \times T$$

Cs: solubility D: diffusion coefficient S: surface area of solid
V: volume of solution δ: the thickness of diffusion layer r: diameter of a particle
δ: the thickness of diffusion layer η: viscosity of solution R: gas constant
T: absolute temperature N: Avogadro's constant

This is Nernst-Noyes-Whitney formula. This formula stands for the dissolution speed, and it can be applied for a certain substance and a solution of that.

Limonene solution of polystyrene is a kind of colloid solution. Therefore, strictly speaking, we cannot say that polystyrene is actually dissolved by limonene. Rather, it is disassembled. So first, we decided to assume that this formula can be applied to the relationship between limonene and polystyrene. If this hypothesis is true, the graph of the relationship between time and dissolved math can be explained in the formula below.

$$y \approx m - me^{-nx} \cdots ①$$

y: dissolved   mass x: time

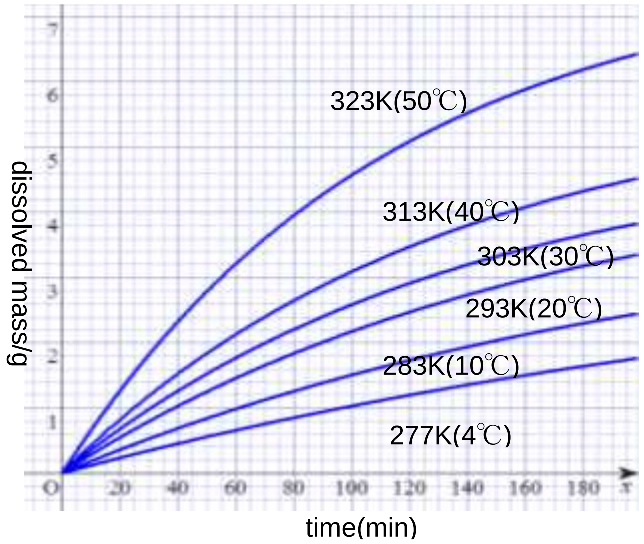
This formula can be drawn from (∗) by the operation below. If our assumption is true, we can find the value of each factor in (∗) from the coefficient of ①,the formula above.

$$m = Cs$$

$$n = \frac{DS}{V\delta}$$

6. Result of experiment1

As the temperature rises, both solubility and dissolution speed go up(【figure5】). Moreover, as the time passes, dissolution speed goes down under every temperature. Finally, as the temperature goes down, the viscosity of solution goes up, though this is based only on observation, not a numerical result.



▲【figure5】 relationship between time and dissolved

By finding approximation formula with the app「grapes(ver7.71)」,the relationship between time and dissolved mass can be explained by the formula which is the same as ①. The value of m and n in ① under each temperature are below(【table1】).

▼【table1】 the value of m and n

	temperature	m	$n(\times 10^{-5})$
A	4℃	3.66	5.50
B	10℃	4.08	7.67
C	20℃	4.81	1.00
D	30℃	5.03	12.0
E	40℃	5.80	12.7
F	50℃	7.75	14.8

7. Consideration of experiment1

We can say that (*) can be applied to the relationship between polystyrene and limonene.

7-1. the value of m

The value of m stands for solubility in (*) and the value goes up as the temperature of solution goes up(【table2】).

▼【table2】 solubility under each temperature

	temperature	solubility (g/60mL)
A	4℃	3.66
B	10℃	4.08
C	20℃	4.81
D	30℃	5.03
E	40℃	5.80
F	50℃	7.75

Typically, the solubility curve can be expressed by the formula below.

$$\log\left(\frac{Cs_2}{Cs_1}\right)=\frac{\Delta H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

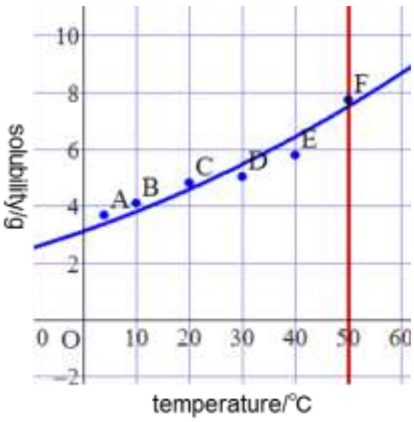
Cs_1: solubility at temperature T_1 Cs_2: solubility at temperature T_2
R: gas constant ΔH: the heat of dissolution

Using this formula, we can say that the solubility of polystyrene to limonene can explain in the approximation formula below.

$$Cs \approx 3.12\times e^{1550\left(\frac{1}{273}-\frac{1}{T}\right)} \quad \cdots②$$

Note: We used the app「grapes(ver7.71)」for approximation.

▼【figure6】 solubility curve
Note: this red line is flash point of limonene. (50℃)

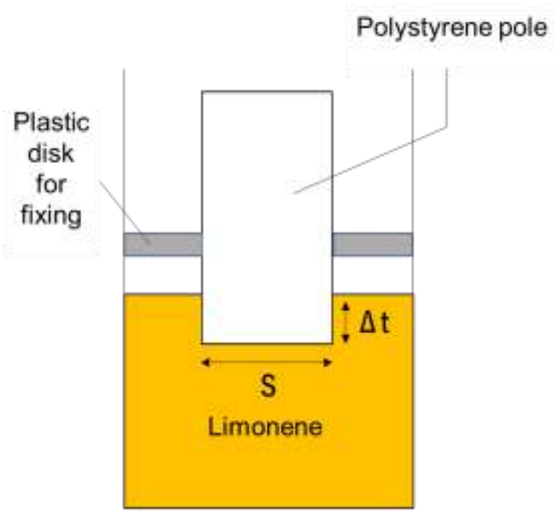


7-1. the value of n

The value of n stands for the right part of the formula below in the (＊).

$$n = \frac{SRT}{6\pi VNr\eta\delta}$$

R, N are constant values, and V, T are fixed through each experiment. In addition, we can say that S is also fixed through each experiment, because the density of polystyrene is so small in comparison with that of limonene that the area of polystyrene touching with limonene is constant (【figure7】). Namely, Δt in the【figure7】is very small.



▲【figure7】 the area of polystyrene touching with limonene

So, we calculated the value of $r\eta\delta$, omitting R, N, V, T, S from the value of n. The value of $r\eta\delta$ goes down as the temperature of the solution goes up(【table3】). R is constant despite temperature, so we consider about the change of η and δ under different temperatures.

▼【table3】 the value of $r\eta\delta$ under each temperature

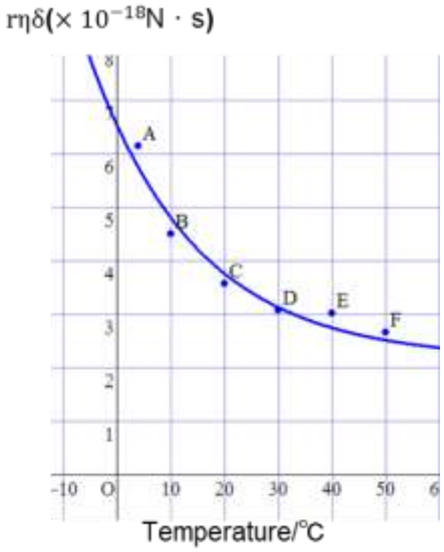
	temperature	$r\eta\delta(\times 10^{-18})$
A	4℃	6.14
B	10℃	4.50
C	20℃	3.58
D	30℃	3.08
E	40℃	3.01
F	50℃	2.66

7-2(Ⅰ). Change of η due to temperature

By the observation of the experiments, it was clear that the higher the temperature of the solution was, the lower the viscosity became. The viscosity generally decreases exponentially with increasing temperature (Reference [5]). Since rηδ also shows a similar decreasing tendency (【figure8】), the decrease of viscosity can be one of the causes of decrease of rηδ. The following formula is an approximation formula of 【figure8】.

$$r\eta\delta \approx 0.7 \times e^{-0.05\,(T-310)} + 2.16$$

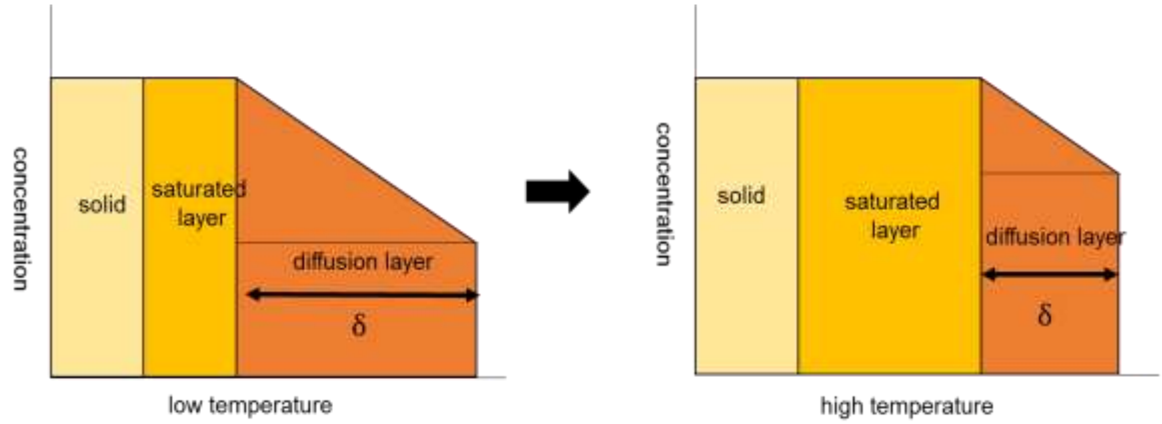
▼【figure8】 the value of rηδ under each temperature



7-2 (Ⅱ). Change of δ due to temperature

The diffusion layer is a layer between a high-concentration part and a low-concentration part in the solution, and δ is the thickness of that layer(【figure9】). When there is a solid in the solution, the concentration in the solution is not strictly uniform. The vertical axis of 【figure9】 represents the concentration of the solution, and the horizontal axis represents the distance from the solid. The closer it is to a solid, the higher the concentration of the solution is, and vice versa.

We considered that when the temperature of the solvent is higher, the saturated layer becomes wider, so that the value of δ, the thickness of the diffusion layer becomes smaller. It is because the convection becomes more active than when the temperature is lower. This may also contribute to the decrease of rηδ.



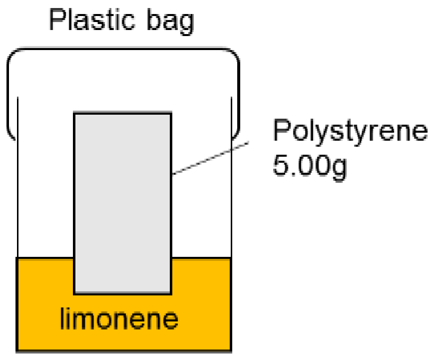
▲【figure9】 the change of diffusion layer due to temperature

8. Experiment 2

In experiment1, we found that the relationship between time and dissolved mas can be represented by ①. Next, we did an experiment to formulate each element in (∗).
First, we examined whether solubility can be expressed by ②, this time experimentally.

[1] Prepare 60ml limonene in a beaker.
[2] Put 5.0g polystyrene into [1].
[3] Wrap the beaker of [2] with a plastic bag and put it into a refrigerator (Mitsubishi Electric Corporation, MR-H26M-T) with thermometer.
[4] After 24 hours, record the temperature of the thermometer and mass of polystyrene which remains at the beaker.

Note: When we measured the temperature of the refrigerator in advance, the temperature was 8℃. According to the solubility curve we calculated(【figure6】), the theoretical solubility at 8℃ was 3.67g, so we used 5.00g polystyrene so that not all polystyrene would be dissolved.
Note: we used a plastic bag to cover the beaker(【figure10】) because limonene is volatile.



▲【figure10】 experiment2

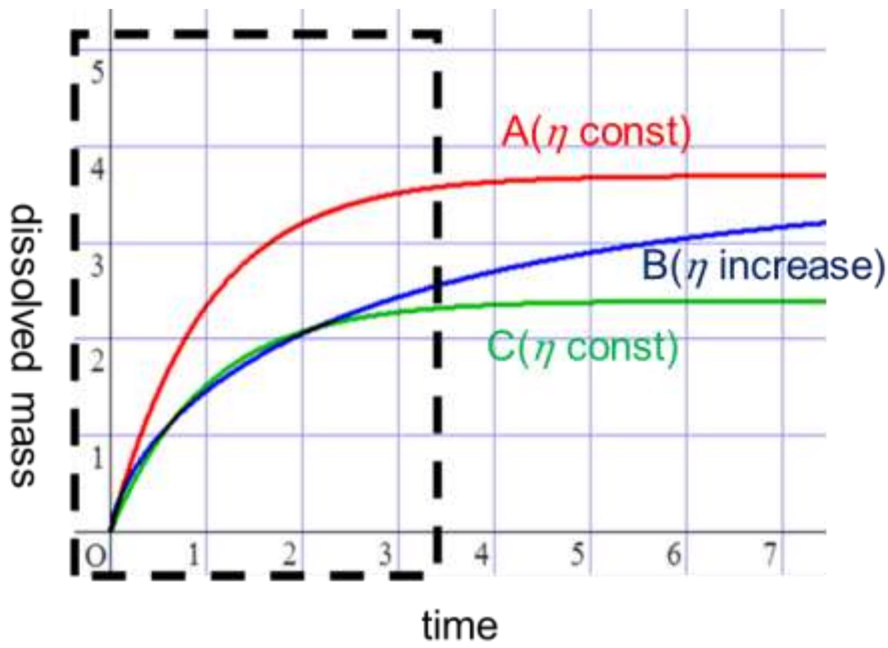
9. Result of experiment2

All polystyrene we prepared had already been dissolved within 24 hours. It means that about 1.4 times as much polystyrene as theoretical solubility was dissolved.

10. Consideration of experiment2

In **7-2(I). Change of η due to temperature**, we thought that η (viscosity of solvent) did not change under a constant temperature. However, when we observed limonene solution after experiment2, its viscosity had clearly become stronger than that before experiment2. So, we considered that the viscosity becomes stronger as dissolved mass increases.

By the way, please look at （＊） again. This shows the slope on time-dissolved mass graph. If the value of η increases as dissolved mass(C) increases in experiment1, the slope on this graph becomes smaller rapidly than when η is constant. As a result, the value of dissolved mass can be underestimated in comparison with an actual value. We might have estimated solubility smaller than actual solubility in this way.



▲【figure11】 the models of time-dissolved mass graphs(η const and η increase)

For example, these three curves in【Figure11】are based on （＊）. The solubility in curve (A) and curve (B) are the same value, and the solubility in curve (C) is smaller than that of curve (A) and curve (B). However, in curve (B), the value of η increases in proportion to dissolved mass, while the value of η in curve (A) and curve (C) are constant. When we look at inside the black dashed frame, the value of dissolved mass in curve (B) and curve (C) seem to settle the same value. In other words, we estimate the solubility in curve (B) smaller than actual value. It means that we underestimate the solubility when we only look at the beginning of experiments. We might have taken the same mistake.

11. Summary of experiment1, 2

We can say that the relationship between limonene and polystyrene is expressed by Noyes-Whitney Formula. However, even though we knew characteristic of each element in this formula, we must research and consider how much they depend on temperature or time. As for the value of δ, thickness of diffusion layer, it might change due to the shape of container or beaker.

12. Prospects

・Investigate changes in η (viscosity of the solution) due to temperature and changes due to an increase in the dissolved mass of polystyrene.

・δ(thickness of the diffusion layer) might change depending on the container used for experiments, so the dependence on the shape of containers must be investigated.

・As for experiment 2, this time, there is nothing other than a refrigerator that could keep the temperature of the solution constant for a long time, so the experiment was only be conducted at 8.0℃. We will experiment at other temperatures to draw an accurate solubility curve.

・In this experiment, we changed the temperature of the solution and observed the change in the dissolution speed. In the future, in order to bring this recycling method closer to practical use, we are planning to conduct experiments by changing the purity of limonene. This is because using limonene extracted from citrus fruits for recycling is ideal, and that limonene is thought to contain impurities. If high efficiency of dissolution can be achieved even with low-purity limonene, the cost of purification limonene can be saved.

・Experiments 1 and 2 took a very long time. We are also looking for more efficient and accurate experimental methods.

・It is said that more than 90% of the dissolved polystyrene and the limonene used for recycling can be reused. We will investigate how many times polystyrene can be reused, and how dissolving ability of limonene change when it is reused.

13. Acknowledgments

We would like to express our sincere gratitude to Professor Kazushi Oda of Japan Advanced Institute of Science and Technology and the teachers of Ishikawa Prefectural Kanazawa Izumigaoka High School for their guidance in advancing this research. Thank you for your cooperation.

14. Reference

[1] Plastic Waste Management Institute. “Plastic Information Bureau：What’s new”. http://www.pwmi.or.jp, (2020-11-16).

[2] Japan Expanded Polystyrene Association. “Recycling results”. https://www.jepsa.jp/recycle/results.html, (2020-11-16).

[3] The dissolution and its speed of the substitute http://yaku-tik.com, (2020-9-16)

[4] Breakthrough system to disposal polystyrene-the recycling plant in Kochi which uses orange oil ”limonene” http://www.iyoric.jp, (2020-5-20)

[5] The relationship between the temperature and viscosity of liquid Heisin Mohno Dispenser http://www.mohno-dispenser.he/compass/compass03.html, (2021-2-17)