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Dissolution of polystyrene into *p*-cymene and related substances in tree leaf oils

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Abstract We examined the dissolution of polystyrene into *p*-cymene and related substances to develop an alternative method for the recycling of expanded polystyrene. The dissolving power of *p*-cymene [212.0 g (100 g solvent)$^{-1}$] to polystyrene at 50°C compared favorably with those of 2-*p*-cymenol [156.7 g (100 g solvent)$^{-1}$], (*R*)-limonene and its structural isomers [181.7–197.1 g (100 g solvent)$^{-1}$], and *Abies* leaf oil [84.7 g (100 g solvent)$^{-1}$]. The favorable solubility of polystyrene into *p*-cymene can be explained by the solubility parameter. *p*-Cymene and polystyrene can be recovered almost quantitatively from the polystyrene solution by simple steam distillation.

Key words Recycling of polystyrene · Tree leaf oil · *p*-Cymene · Solubility parameter

Introduction

Expanded polystyrene is widely used as food trays, packaging materials, or adiabators because of its excellent shock-absorbing property, low thermal conductivity, and light weight. In Japan, the output of expanded polystyrene in 2007 amounted to 182,000 tons. Although the recycling rate of plastics has been currently improved, the material recycling of expanded polystyrene is still at the 50% level in Japan. Increase in the recycling rate of plastics is an important strategy for reducing our dependence on petroleum-derived chemicals. The most commonly employed process for the material recycling of expanded polystyrene includes shrinking by heated air or frictional heat. However, undesirable oxidative degradation of polystyrene occurs during the thermal shrinking process.[1]

Recently, great interest has been focused on an alternative method for shrinking expanded polystyrene using *Citrus* peel oil,[1] of which the main component is a naturally occurring monoterpene, (*R*)-limonene. Although *Citrus* peel is a renewable resource, a pile of the peel corresponding to about 10,000 oranges is necessary for extracting 1 l of oil.

p-Cymene is an aromatic hydrocarbon that occurs widely in tree leaf oils.[2–5] Its chemical structure is similar to that of styrene. Generally, a good solvent for a certain polymer has a solubility parameter value close to that of the polymer, i.e., the structural similarity between a solute and a solvent favors solubility.[6] Recently, we have found that polystyrene was dissolved into *p*-cymene and *Abies* leaf oil at ambient temperature. Certain foliage is, therefore, a potential resource for the recycling solvent of expanded polystyrene. First, we examined the solubilities of polystyrene into *p*-cymene and its related substances in tree leaf oil, and calculated their solubility parameter and apparent activation energy (E_a) for the dissolution, to explain the relationship between the chemical structure of the solvent and the dissolution behavior of polystyrene.

Experiments

Materials

p-Cymene, 2-*p*-cymenol (carvacrol), (*R*)-limonene, α-terpinene, and terpinolene were purchased from Tokyo Chemical Industry (Tokyo, Japan). *Abies* leaf oil was prepared by steam distillation of the fresh leaves of *Abies sachalinensis* Masters, which were collected in the Ainonai forest of Sato Forestry Co. (Kitami, Japan) in August 2006. Polystyrene used for the dissolution experiments was obtained from Sigma-Aldrich (St. Louis, MO, USA). Average molecular weights of the polystyrene were measured by gel permeation chromatography (GPC) in chloroform referenced to standard polystyrene samples (product # SM-105; Showa Denko, Tokyo, Japan).

For the dissolution experiments, polystyrene films were prepared. Commercial polystyrene pellets were pressed under 20 MPa at 260°C for 5 min, then cooled to ambient

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temperature. Polystyrene disks with a diameter of 5 mm (average weight, 2.30 ± 0.03 mg) were punched out from the film.

Dissolution experiments

A polystyrene disk was put in a test tube with 0.2 ml solvent. The test tube was sealed by a silicon rubber stopper and then placed in a shaking thermostatic water bath. The shaking speed used throughout the study was 120 strokes min^{-1}. The dissolution of polystyrene was judged by visual and/or crossed polarity microscopic observations. For the solubility experiments, when the disk in the test tube disappeared within 24 h, another disk was added to the solution.

Viscosities of the polystyrene solutions

The steady shear viscosity of 5% of the polystyrene solutions was measured at 40°C on a Brookfield digital cone and plate rheometer model-III+ equipped with a thermocontroller. The radius and angle of the cone were 12 mm and 0.05°, respectively. The steady shear rate was $100\ s^{-1}$. The average of three times of measurements was adopted for each sample.

Recovery of the solvent and polystyrene

To examine the recovery of the solvent and polystyrene, polystyrene pellets (0.2 g) were dissolved in 2 ml solvent. Water (50 ml) was added to the solution, and then the mixture was subjected to steam distillation for 3 h. The recovery yield of the solvent was evaluated by the volume. All measurements were replicated five times, and the means and SDs of the analytical data were obtained.

Results and discussion

It is known that the structural similarity between solute and solvent favors solubility.[6] The chemical structure of *p*-cymene, an aromatic component of *Abies* leaf oil,[5] is similar to that of polystyrene. Hence, polystyrene would mix well with *p*-cymene or *Abies* leaf oil. In the preliminary experiments, a small block of a commercial food tray made of expanded polystyrene (20 × 20 × 4 mm) was immediately dissolved in a few drops of *p*-cymene or (*R*)-limonene at ambient temperature. We first examined the solubility of polystyrene into *p*-cymene and its related substances (Fig. 1). The experimental results are listed in Table 1. One hundred grams of *p*-cymene dissolved 212.0 g polystyrene at 50°C. This dissolving power was higher than those of (*R*)-limonene and its structure isomers, such as α-terpinene and terpinolene. No remarkable difference was observed among (*R*)-limonene, α-terpinene, and terpinolene, so that the position of a double bond would not affect the dissolving power greatly. The introduction of a hydroxyl group into *p*-cymene resulted in a significant decrease in the solubility.

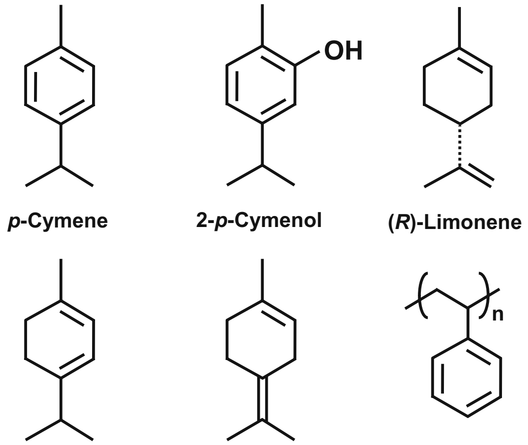

Fig. 1. Chemical structures of solvents and solute used in these experiments

Table 1. Solubility of polystyrene into *p*-cymene and its related substances at 50°C

Solvent	Solubility[a] [g (100 g solvent)$^{-1}$]
p-Cymene	212.0 ± 0.2
2-*p*-Cymenol	156.7 ± 0.2
(*R*)-Limonene	181.7 ± 0.1
α-Terpinene	197.1 ± 0.2
Terpinolene	191.4 ± 0.2
Abies leaf oil	84.7 ± 0.2

[a] Mean ± SD, $n = 5$

For further investigation on the relationship between the chemical structure of the solvents and the dissolution behavior of polystyrene, E_a for the dissolution and solubility parameter (δ) of the solvents were evaluated. The time (t) required for the dissolution of a polystyrene disk (2.30 ± 0.03 mg) was measured at temperatures in the range 30°–70°C (Table 2). The E_a was obtained from the slope of the Arrhenius plot of ln t versus the inverse of thermodynamic temperature. It is known that the rate constant decreases with increasing the E_a and increases with increasing temperature.[7] The E_a of *p*-cymene was similar to that of (*R*)-limonene. On the other hand, the E_a of 2-*p*-cymenol was remarkably larger than that of the other solvents, suggesting that 2-*p*-cymenol has higher temperature dependence on the dissolution of polystyrene than *p*-cymene.

It has been found that a good solvent for a solute has a δ value close to that of the solute.[6] The δ values of *p*-cymene, 2-*p*-cymenol, (*R*)-limonene, α-terpinene, and terpinolene were calculated according to the method of Hoftyzer and Van Krevelen.[8] As shown in Table 2, the δ values of *p*-cymene ($14.6\ MPa^{1/2}$) and 2-*p*-cymenol ($19.4\ MPa^{1/2}$) explain their dissolution power for polystyrene. Generally, the occurrence of a hydroxyl group in a solvent molecule causes reduction of accessibility to the

Table 2. Time required for dissolution (s), apparent activation energy (E_a) for polystyrene dissolution and solubility parameter (δ)

Solvent	Time required for dissolution (s)[a]					E_a (kJ mol^{-1})	δ (MPa$^{1/2}$)
	30°C	40°C	50°C	60°C	70°C		
p-Cymene	215 ± 2	149 ± 1	109 ± 1	85 ± 1	66 ± 2	25.1	14.6
2-*p*-Cymenol	11,458 ± 51	3,830 ± 16	1,991 ± 4	829 ± 4	403 ± 2	71.2	19.4
(*R*)-Limonene	255 ± 2	184 ± 1	145 ± 1	102 ± 2	85 ± 1	24.1	15.2
α-Terpinene	263 ± 2	191 ± 1	147 ± 1	114 ± 3	90 ± 3	23.1	14.9
Terpinolene	228 ± 2	173 ± 2	134 ± 1	103 ± 2	74 ± 2	23.9	15.7
Abies leaf oil	2,507 ± 8	964 ± 2	665 ± 1	329 ± 1	184 ± 2	54.6	–[b]
Polystyrene	–	–	–	–	–	–	14.5

[a] Mean ± SD, $n = 5$
[b] The δ value is not given because *Abies* leaf oil is a mixture of many essential oil components

Table 3. Steady shear viscosities of 5% polystyrene solutions[a]

Solvent	Viscosity (cP)
p-Cymene	2.3
2-*p*-Cymenol	31.8
(*R*)-Limonene	2.5
Abies leaf oil	2.9

[a] The measurements were carried out at 40°C
The steady shear rate was 100 s^{-1}

hydrophobic polymer matrix. The reduced dissolution power of *Abies* leaf oil was explained by the existence of acyclic monoterpene alcohols such as geraniol and linalool,[5] because they are poor solvents for polystyrene.

Viscosity of the solutions is an important factor for the dissolution of polystyrene, because high viscosity of the solution decreases the mobility of solute and solvent in the system and prevents the solute from diffusing in the solvent. Noguchi et al.[1] reported that, when a small amount of ethanol was added to the (*R*)-limonene solution containing 20% polystyrene by weight, the viscosity of the solution was lowered and the rate of dissolution was greatly improved. Table 3 shows the steady shear viscosities of the solutions containing 5% polystyrene by weight. The 2-*p*-cymenol solution exhibited relatively high viscosity compared with the other solutions. Such high viscosity would delay the dissolution time of polystyrene. As the result, the dissolving power of 2-*p*-cymenol would be poor compared with the other solvents.

To evaluate the recycling system for expanded polystyrene, the molecular weights of the polystyrene recovered and the recovery yield of the solvents from the solutions were studied (Table 4). The solvents were mostly recovered by steam distillation of 10% (w/v) of the solutions. On the other hand, the number-average molecular weight of the polystyrene decreased from 1.31×10^5 (virgin polystyrene) to 1.10×10^5 (polystyrene recovered from the 2-*p*-cymenol solution), suggesting that certain degradation occurred slightly. The degradation may be caused by oxygen radicals from air during the steam distillation.[9] The use of radical scavengers prevents undesirable degradation of polystyrene.

In conclusion, *p*-cymene, which is widely distributed in tree leaf oils, can be used as an alternative shrinking agent for expanded polystyrene. Its dissolving power for polystyrene compared favorably with those of (*R*)-limonene and its structural isomers. The introduction of a hydroxyl group into *p*-cymene resulted in a significant decrease in the solubility. The favorable solubility of polystyrene into *p*-cymene can be explained by the solubility parameter. *p*-Cymene and polystyrene are recovered almost quantitatively by simple steam distillation of the solution.

Table 4. Recovery yield of solvents and average molecular weights of polystyrene recovered by steam distillation

Solvent	Recovery yield of solvent (%)[a]	Molecular weight of polystyrene recovered		
		M_n[b]	M_w[c]	Dispersion
p-Cymene	96.3 ± 0.4	1.29×10^5	2.30×10^5	1.78
2-*p*-Cymenol	92.0 ± 0.9	1.10×10^5	2.15×10^5	1.95
(*R*)-Limonene	94.9 ± 1.1	1.20×10^5	2.17×10^5	1.81
α-Terpinene	95.5 ± 1.2	1.27×10^5	2.22×10^5	1.75
Terpinolene	92.3 ± 0.9	1.22×10^5	2.26×10^5	1.85
Abies leaf oil	89.5 ± 0.6	1.25×10^5	2.33×10^5	1.86
Not treated	–	1.31×10^5	2.53×10^5	1.93

[a] Mean ± SD, $n = 5$
[b] Number-average molecular weight
[c] Weight-average molecular weight

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