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Recycling of Expanded Polystyrene Using Natural Solvents

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1. Introduction

The recycling of natural resources and waste products is the most important process in the concept of green chemistry. Recently, the utilization of biomass has been a significant topic, whereas the recycling of petroleum resources must receive similar attention. Expanded polystyrene (EPS) is widely used in packing and building materials and for electrical and thermal insulation owing to the light weight and low thermal and electrical conductivities. The porosity of EPS is very high such as 98% of the apparent volume is porous. At present, over 2 million tons of EPS are produced in the world per year [1], and the rate of the material recycling is relatively high among commodity plastics [2].

For the recycling of EPS, melting [2,3] or solvent treatment [4,5] is required to reduce the volume and to be reshaped subsequently, as illustrated in Figure 1. The melting process is simple, but brings about some chemical degradation and cannot avoid debasing the quality of the original polystyrene (PS), so the solvent treatment is, in many respects, more desirable for an effective recycling system. Although there are various solvents for PS, for example, hydrocarbons, alkyl halides, aromatics, esters, and ketones, petroleum-based solvents are not favorable to the global environment. Limonene, which is a component of citrous oils, was derived from the above concept, and it is a pioneer of natural solvents for EPS [6-8]. Lately, the recycling of EPS using limonene has been realized in practical use with a semi-industrial scale, however, peel corresponding to approximately 1,000 oranges is necessary to extract 100 mL of limonene [9]. Except for limonene, there is few report on the natural solvents for EPS. This chapter is mainly focused on the dissolution of PS in naturally abundant monoterpenes including limonene, particularly, the relationship between the chemical structure and dissolving power for PS. In addition, the properties of the PS recycled by using these solvents are also described, compared with those of the original PS.

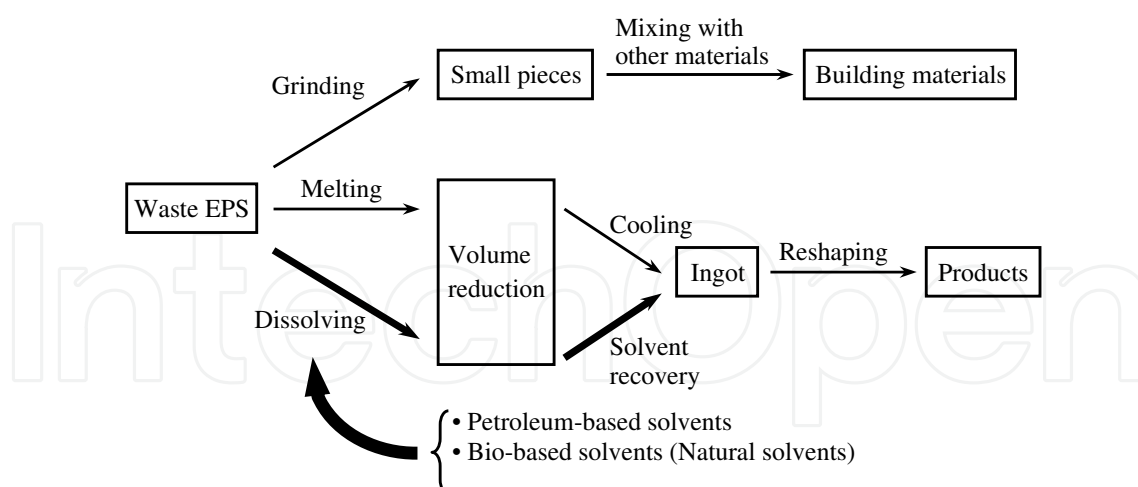


Figure 1. Material recycling system of EPS.

2. Naturally occurring monoterpenes and their dissolving power for PS

Hattori et al. [10] paid attention to the fact that, as limonene is one of terpenes, other monoterpenes and terpenoids are expected to dissolve PS as well. Terpene is a biomolecular hydrocarbon whose structural backbone possesses an isoprene unit. Corresponding to the number of an isoprene unit, they are called monoterpene (C10), sesquiterpene (C15), diterpene (C20), sesterterpene (C25), and so forth. Many monoterpenes are liquid at room temperature and main components of essential oils. In particular, the leaf oils of *Abies sachalinensis* and *Eucalyptus* species, in which the growth is comparatively fast, may be suitable biomass because they are not utilized effectively at present and contain many monoterpenes. Table 1 summarizes some liquid monoterpenes and terpenoids selected from the viewpoint of content rate in their leaf oils [11-13]. Both are significantly different. *d*-Limonene is much contained in *Abies sachalinensis*, but a little in *Eucalyptus*. The largest amount of bornyl acetate in *Abies sachalinensis* is not contained in *Eucalyptus*. In contrast, 1,8-cineole occurs abundantly in *Eucalyptus*, whereas does not occur at all in *Abies sachalinensis*.

First, some structural isomers and analogues of *d*-limonene, as shown in Figure 2, were studied on the dissolving power for PS [10]. The experimental method is as follows. A known weight of a small piece of commercial PS film with a number-average molecular weight (\bar{M}_n) of 1.2×10^5 was put in 0.5 mL of each terpene at 50 °C, and the behavior of PS was observed by a polarizing microscopy under crossed nicols. The dissolution was judged from the disappearance of birefringence of the PS piece. The additional piece, if necessary, was put after complete dissolution was achieved. In Table 2, the dissolving power of the terpenes is listed as the weight of the PS dissolved per 100 g of each terpene. All these terpenes are capable of dissolving more than 120 g of PS per 100 g of them. The values are greater than that of toluene, which is one of the petroleum-based solvents for PS. These six terpenes except for *p*-cymene are structural isomers with different locations of a C=C bond, so they would have similar dissolving power

| Terpene and terpenoid | Content rate (%) ^a | |
|-----------------------|-------------------------------|-------------------|
| | <i>Abies sachalinensis</i> | <i>Eucalyptus</i> |
| Bornyl acetate | 27.0 | 0 |
| <i>d</i> -Limonene | 22.6 | 3.1 |
| β -Phellandrene | 15.6 | 0 |
| α -Pinene | 13.3 | 37.9 |
| β -Pinene | 9.7 | 0.5 |
| Myrcene | 1.9 | 0.4 |
| <i>p</i> -Cymene | 0.4 | 2.9 |
| 1,8-Cineole | 0 | 29.9 |

a) The percentage in 100 mL of the leaf oil measured by GC-MS [11-13].

Table 1. Components in the leaf oils of *Abies sachalinensis* and *Eucalyptus*.

one another. This result led to a relationship between the structure and dissolving power that the position of a C=C bond does not affect the dissolving power greatly. The solubility of PS in *p*-cymene is remarkably higher than that in other terpenes, because *p*-cymene is, as described later, an aromatics that has a similar chemical structure to PS.

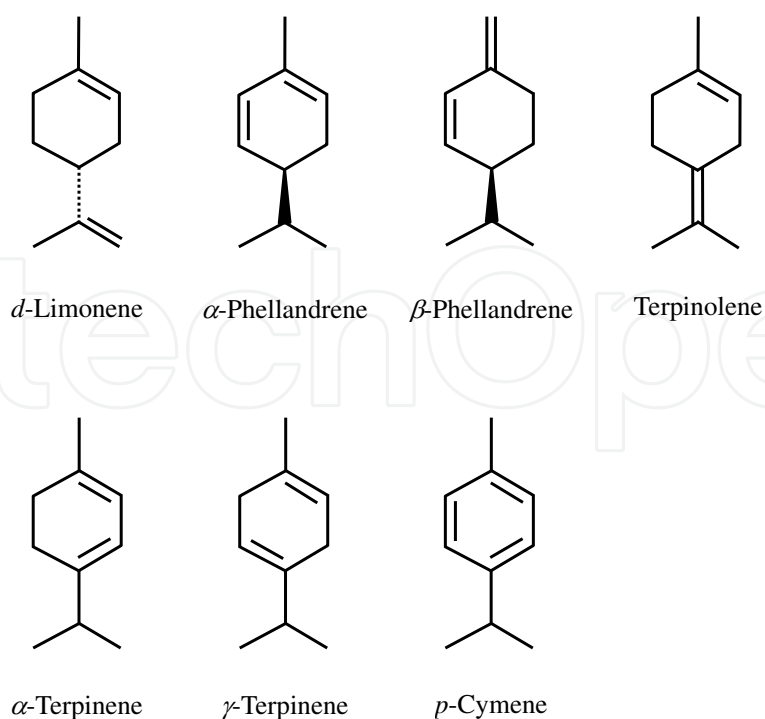


Figure 2. Structure of *d*-limonene and its some isomers and analogues.

| Solvent | Solubility (g/ 100 g · solvent) ^a |
|------------------------|--|
| α -Terpinene | 130 |
| γ -Terpinene | 131 |
| <i>d</i> -Limonene | 127 |
| Terpinolene | 125 |
| α -Phellandrene | 125 |
| β -Phellandrene | 122 |
| <i>p</i> -Cymene | 212 |
| Toluene ^b | 117 |

a) Cited from reference [10].

b) One of the petroleum-based solvents was used for comparison.

Table 2. Solubility of PS in several monoterpenes at 50 °C.

As shown in Table 1, there is a considerable amount of 1,8-cineole in *Eucalyptus* leaf oil. Therefore, the next investigation of the dissolving power of natural solvents for PS went to 1,8-cineole and some related oxygen-containing terpenoids [10,14]. Figure 3 and Table 3 represent the chemical structure of the terpenoids and their dissolving power for PS, respectively.

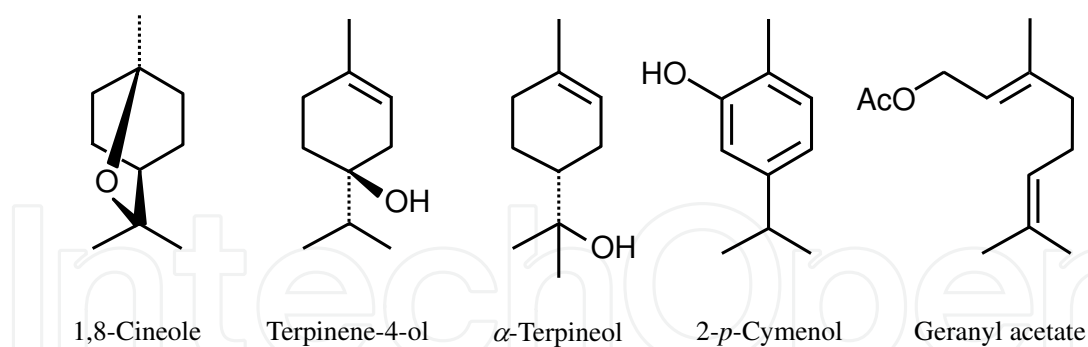


Figure 3. Structure of 1,8-cineole and some oxygen-containing terpenoids.

Generally, a non-polar molecule such as PS does not interact with a polar solvent. Terpinene-4-ol and α -terpineol have such a high polar moiety as a hydroxyl group, hence, the solubilities of PS in them (ca. 40 g/ 100 g · solvent) are lower than those in the corresponding terpinene and terpinolene without a hydroxyl group (ca. 130 g/ 100 g · solvent, Table 2). The oxygen of 1,8-cineole is adopted to not a hydroxyl group, but an ether group. It is suggested that the higher solubility of PS in 1,8-cineole (55 g/ 100 g solvent) than those in terpinene-4-ol and α -terpineol is ascribed to the lower polarity of an ether group compared to a hydroxyl group. The high

| Solvent | Solubility (g/ 100 g · solvent) ^a |
|----------------------|--|
| 1,8-Cineole | 55 |
| Terpinene-4-ol | 39 |
| α -Terpineol | 41 |
| 2- <i>p</i> -Cymenol | 105 |
| Geranyl acetate | 174 |

a) Cited from refereces [10] and [14].

Table 3. Solubility of PS in several oxygen-containing terpenoids at 50 °C.

dissolving power of 2-*p*-cymenol (105 g/ 100 g·solvent), in spite of possessing a hydroxyl group, may be due to the presence of an aromatic ring as mentioned above.

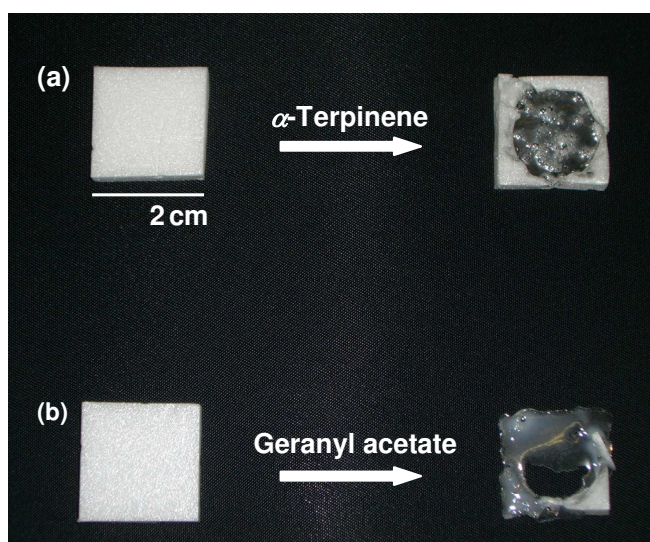


Figure 4. EPS shrunk by α -terpinene (a) and geranyl acetate (b) [10].

Geranyl acetate shows highest dissolving power of 174 g per 100 g of it. Figure 4 demonstrates the appearance of dissolving EPS by α -terpinene (a) and geranyl acetate (b) [10]. Geranyl acetate is apparently more powerful than α -terpinene concerning the ability to shrink EPS. It seems that the high dissolving power of geranyl acetate is based on its flexible linear structure, which is more accessible to the inside of bulk PS compared with the cyclic terpenes in Table 2. Therefore, the dissolving power of several acyclic monoterpenes was studied for the confirmation of that. Geranyl acetate, citronellyl acetate, and myrcene are found in the essential oils of *Picea* genus and others [11], and citral and citronellal are components of citrus oils [15]. As shown in Table 4, geranyl acetone, geranyl formate, and citronellyl acetate have similar dissolving power as high as geranyl acetate has.

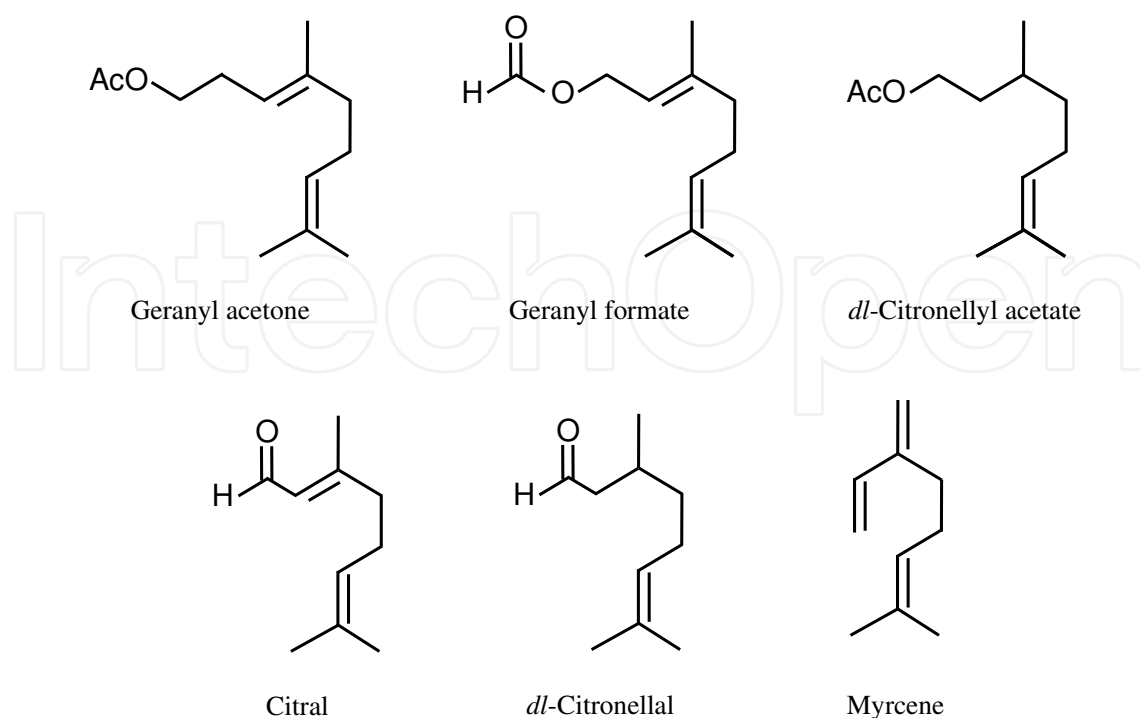


Figure 5. Structure of several acyclic terpenes and terpenoids.

| Solvent | Solubility (g/ 100 g · solvent) ^a |
|---------------------|--|
| Geranyl acetone | 160 |
| Geranyl formate | 175 |
| Citronellyl acetate | 156 |
| Citral | 109 |
| Citronellal | 125 |
| Myrcene | 101 |

a) Partly cited from reference [10].

Table 4. Solubility of PS in several acyclic terpenoids at 50 °C.

These values are higher than those of typical cyclic monoterpenes in Table 2. The relatively low dissolving power of citral and citronellal compared with acyclic esters would be due to the occurrence of the terminal aldehyde group of a polar moiety that causes the reduction of accessibility to the hydrophobic matrix of PS. Unexpectedly, myrcene does not show very high dissolving power of 101 g per 100 g of it although it is a non-polar hydrocarbon. The structure of the terminal conjugated diene is probably not so flexible as to penetrate it into PS matrix.

These results indicate clearly that flexible linear terpenes have higher dissolving power for PS than cyclic terpenes have.

A series of these systematic experimental results causes one fundamental question: how much dissolving power do the essential oils themselves have? *Abies* oil can be easily prepared by refluxing for 6 h in water and subsequent steam distillation of the leaves of *Abies sachalinensis* [14]. *Eucalyptus* oil is commercially available from Tokyo Chemical Industry, Inc., Japan. The solubilities of PS in the *Abies* and *Eucalyptus* oils were 85 g and 96 g per 100 g of them [14], respectively, as shown in Table 5. According to the reports of Yatagai et al. [11,12], *Abies* leaf oil contains 27% of bornyl acetate and 23% of pinenes whose structure and dissolving power are as follows.

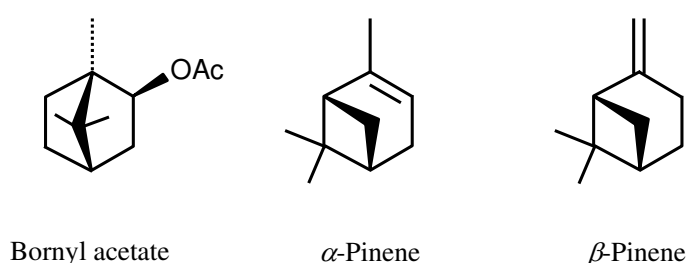


Figure 6. Structure of bornyl acetate and pinenes.

| Solvent | Solubility (g/ 100 g · solvent) ^a |
|--------------------------------------|--|
| <i>Abies</i> leaf oil | 85 |
| <i>Eucalyptus</i> oil | 96 |
| Bornyl acetate | 67 |
| α -Pinene | 44 |
| β -Pinene | 48 |
| a) Partly cited from reference [10]. | |

Table 5. Solubility of PS in essential oils and several bicyclic terpenes at 50 °C.

The solubilities of PS in bornyl acetate and both pinenes are less than half of those in limonene isomers. Bornyl acetate and the pinenes have a bulky bicyclic structure, which is likely to be disadvantageous to penetrate into PS. As a result, the *Abies* leaf oil containing approximately 50% of these three terpenes in total does not have so high dissolving power for PS. Since *Eucalyptus* oil also contains such bicyclic terpenes as 30% of 1,8-cineole and 38% of α-pinene, it is not a very strong solvent for PS itself. However, both oils still have dissolving power of nearly 100 g for PS per 100 g of them, so that they will be a favorable solvent for PS recycling.

3. Relationship between solubility parameter and dissolving power of monoterpenes

As a general standard for the judgment that a given solute is soluble or insoluble in a solvent, there is a method to compare the "solubility parameter" of the solute with the solvent. Hildebrand first devised the theory of this concept [16], and afterward Hansen [17], Barton [18], and Hoftyzer and Krevelen [19,20] et al. have developed this theory. The solubility parameter (δ) of a substance is defined as:

$$\delta = \sqrt{\frac{E_{\text{coh}}}{V}} \quad (1)$$

where E_{coh} and V are the cohesive energy (=vaporization energy) and molar volume of the substance, respectively. The V is calculated from the molecular weight and density of the substance. The E_{coh} can be obtained experimentally for a volatile substance, but is usually derived from theoretical approach. Hansen [17] considered that E_{coh} is consisting of three types of energies derived from the following interaction forces:

$$E_{\text{coh}} = E_{\text{d}} + E_{\text{p}} + E_{\text{h}} \quad (2)$$

where E_{d} , E_{p} , and E_{h} are the energy of dispersion forces, polar forces, and hydrogen bonding, respectively. Then, Equation (1) is modified using the corresponding solubility parameter components, δ_{d} , δ_{p} , and δ_{h} to each force as follows:

$$\delta = \sqrt{\delta_{\text{d}}^2 + \delta_{\text{p}}^2 + \delta_{\text{h}}^2} \quad (3)$$

Taking account of these intermolecular interactions, Hoftyzer and Krevelen [19] expressed their components such as:

$$\delta_{\text{d}} = \frac{\sum F_{\text{d}_i}}{V}, \delta_{\text{p}} = \frac{\sqrt{\sum F_{\text{p}_i}^2}}{V}, \text{ and } \delta_{\text{h}} = \frac{\sqrt{\sum E_{\text{h}_i}}}{V} \quad (4)$$

where F_{d_i} , F_{p_i} , and E_{h_i} are the parameter of dispersion forces, polar forces, and hydrogen bonding, respectively, reflecting the contribution of structural groups of the substance. Among

the group contribution parameters established by Hoftyzer and Krevelen [20], those related to terpenes are shown in Table 6.

| Structural group | $F_{d_i} (\text{J}^{1/2} \cdot \text{m}^{3/2} \cdot \text{mol}^{-1})^a$ | $F_{p_i} (\text{J}^{1/2} \cdot \text{m}^{3/2} \cdot \text{mol}^{-1})^a$ | $E_{h_i} (\text{J} \cdot \text{mol}^{-1})^a$ |
|-------------------|---|---|--|
| $-\text{CH}_3$ | 0.42 | 0 | 0 |
| $-\text{CH}_2-$ | 0.27 | 0 | 0 |
| $-\text{CH}-$ | 0.08 | 0 | 0 |
| $-\text{C}-$ | -0.07 | 0 | 0 |
| $=\text{CH}_2$ | 0.40 | 0 | 0 |
| $=\text{CH}-$ | 0.20 | 0 | 0 |
| $=\text{C}-$ | 0.07 | 0 | 0 |

a) Cited from reference [20].

b) If two identical polar groups are present in a symmetrical position, the value of δ_p must be multiplied.

Table 6. Group contribution parameters related to terpenes.

| Structural group | $F_{d_i} (\text{J}^{1/2} \cdot \text{m}^{3/2} \cdot \text{mol}^{-1})$ | $F_{p_i} (\text{J}^{1/2} \cdot \text{m}^{3/2} \cdot \text{mol}^{-1})$ | $E_{h_i} (\text{J} \cdot \text{mol}^{-1})$ |
|---------------------------|---|---|--|
| $-\text{CH}_3 \times 4$ | 1.68 | 0 | 0 |
| $-\text{CH}_2- \times 3$ | 0.81 | 0 | 0 |
| $=\text{CH}- \times 2$ | 0.40 | 0 | 0 |
| $=\text{C}- \times 2$ | 0.14 | 0 | 0 |
| $-\text{COO}-$ | 0.39 | 0.49 | 7000 |
| Sum | 3.42 | 0.49 | 7000 |

Table 7. Group contribution parameters of geranyl acetate.

According to Table 6, the group contribution parameters of geranyl acetate are calculated as shown in Table 7. Since the molecular weight (MW) and density (d) of geranyl acetate are 196.29 g/mol and 0.909 g/cm³, respectively, the molar volume V is estimated to 2.159×10^{-4} m³/mol. Therefore, the solubility parameter components are:

$$\delta_d = \frac{\sum F_{d_i}}{V} = \frac{3.42 \text{ J}^{1/2} \cdot \text{m}^{3/2} \cdot \text{mol}^{-1}}{2.159 \times 10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}} = 15.8 \text{ MPa}^{1/2},$$

$$\delta_p = \frac{\sqrt{\sum F_{p_i}^2}}{V} = \frac{0.490 \text{ J}^{1/2} \cdot \text{m}^{3/2} \cdot \text{mol}^{-1}}{2.159 \times 10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}} = 2.27 \text{ MPa}^{1/2}, \text{ and}$$

$$\delta_h = \sqrt{\frac{\sum E_{h_i}}{V}} = \sqrt{\frac{7000 \text{ J} \cdot \text{mol}^{-1}}{2.159 \times 10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}}} = 5.69 \text{ MPa}^{1/2}.$$

From these components, the solubility parameter of geranyl acetate is found:

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} = 16.9 \text{ MPa}^{1/2}.$$

The calculated δ values of all the terpenes from Table 1 to Table 5 are shown, together with the MW and d , in Table 8. The δ of PS is calculated to be 14.5 MPa^{1/2} from the structure of a repeating unit. Referring to Table 8, the δ values of seven terpenes from α -terpinene to p -cymene are very close (14.7–15.7 MPa^{1/2}), especially the δ of p -cymene is almost the same (14.6 MPa^{1/2}), to that of PS. This fact is in good agreement with the experimental results in Table 2 that these terpenes, particularly p -cymene, dissolve a lot of PS. Although 1,8-cineole and four terpenes from the lower row in Table 8 have similar δ values to that of PS, their dissolving powers for PS are low. The reason for such low dissolving powers might be attributable to a steric effect as mentioned above. Hence, it is concluded that a solubility parameter is not universal because it cannot reflect the steric effect of a solvent molecule upon the δ . According to the same reason, the δ value cannot explain the high dissolving powers of three acyclic terpenoids, geranyl acetate, geranyl formate, and citronellyl acetate. The terpenoids of the alcohols and aldehydes have a reasonable relationship between the δ value and dissolving power.

| Terpenes | MW | d (g/cm ³) | δ (MPa ^{1/2}) ^a |
|------------------------|--------|--------------------------|---|
| α -Terpinene | 136.24 | 0.838 | 14.9 |
| γ -Terpinene | 136.24 | 0.853 | 15.2 |
| d -Limonene | 136.24 | 0.840 | 15.2 |
| Terpinolene | 136.24 | 0.863 | 15.7 |
| α -Phellandrene | 136.24 | 0.846 | 14.7 |
| β -Phellandrene | 136.24 | 0.850 | 15.0 |
| p -Cymene | 134.22 | 0.857 | 14.6 |

| Terpenes | MW | d (g/cm ³) | δ (MPa ^{1/2}) ^a |
|----------------------|--------|--------------------------|---|
| 1,8-Cineole | 154.25 | 0.923 | 15.0 |
| Terpinene-4-ol | 154.25 | 0.927 | 19.1 |
| α -Terpineol | 154.25 | 0.934 | 19.2 |
| 2- <i>p</i> -Cymenol | 150.22 | 0.976 | 19.4 |
| Geranyl acetate | 196.29 | 0.909 | 16.9 |
| Geranyl acetone | 194.32 | 0.873 | 16.8 |
| Geranyl formate | 182.29 | 0.908 | 16.9 |
| Citronellyl acetate | 198.31 | 0.890 | 16.8 |
| Citral | 152.24 | 0.890 | 17.8 |
| Citronellal | 154.25 | 0.855 | 17.4 |
| Myrcene | 136.24 | 0.794 | 15.9 |
| Bornyl acetate | 196.29 | 0.980 | 15.8 |
| α -Pinene | 136.24 | 0.859 | 13.6 |
| β -Pinene | 136.24 | 0.874 | 14.2 |

a) Partly cited from references [10] and [14].

Table 8. Solubility parameter of some terpenes calculated by the Hoftyzer and Krevelen method.

4. Dissolution rate of PS in monoterpenes

When the recycling efficiency of PS is being considered, not only dissolving power but also dissolution rate is one of the important factors on evaluating the performance of a solvent.

| Terpenes | Dissolution Time ^a (sec) | | | | | E_a (kJ/mol) ^b |
|------------------------|-------------------------------------|-------|-------|-------|-------|-----------------------------|
| | 30 °C | 40 °C | 50 °C | 60 °C | 70 °C | |
| α -Terpinene | 545 | 401 | 334 | 262 | 208 | 20.3 |
| γ -Terpinene | 496 | 359 | 289 | 240 | 196 | 19.7 |
| <i>d</i> -Limonene | 519 | 471 | 375 | 283 | 200 | 20.7 |
| Terpinolene | 525 | 425 | 365 | 301 | 248 | 16.0 |
| α -Phellandrene | 390 | 321 | 235 | 166 | 125 | 25.2 |
| β -Phellandrene | 263 | 191 | 147 | 114 | 90 | 23.1 |
| <i>p</i> -Cymene | 215 | 149 | 109 | 85 | 66 | 25.1 |
| 1,8-Cineole | 4,480 | 1,390 | 626 | 478 | 302 | 56.3 |

| Terpenes | Dissolution Time ^a (sec) | | | | | E_a (kJ/mol) ^b |
|----------------------|-------------------------------------|-------|-------|-------|-------|-----------------------------|
| | 30 °C | 40 °C | 50 °C | 60 °C | 70 °C | |
| Terpinene-4-ol | — ^c | 4,430 | 1,810 | 950 | 610 | 59.0 |
| α -Terpineol | 3,025 | 1,289 | 715 | 418 | 344 | 47.7 |
| 2- <i>p</i> -Cymenol | 11,458 | 3,830 | 1,991 | 829 | 403 | 71.2 |
| Geranyl acetate | 719 | 543 | 493 | 424 | 269 | 19.1 |
| Geranyl acetone | 748 | 505 | 451 | 323 | 211 | 25.7 |
| Geranyl formate | 628 | 527 | 325 | 253 | 152 | 30.7 |
| Citronellyl acetate | 869 | 507 | 411 | 292 | 265 | 25.5 |
| Citral | 1,168 | 712 | 490 | 347 | 230 | 34.3 |
| Citronellal | 597 | 380 | 290 | 231 | 150 | 28.2 |
| Myrcene | 435 | 297 | 200 | 165 | 117 | 27.9 |
| Bornyl acetate | 14,900 | 3,660 | 1,590 | 862 | 558 | 69.8 |
| α -Pinene | — ^c | 1,860 | 852 | 600 | 503 | 38.5 |
| β -Pinene | 3,213 | 690 | 366 | 242 | 142 | 63.5 |

a) The average of five times measurements.

b) Partly cited from references [10] and [14].

c) Insoluble.

Table 9. Dissolution time and apparent activation of (E_a) for the dissolution of PS in the terpenes.

Therefore, the dissolution time of PS in each terpene was measured at several different temperatures, and then the apparent activation energy (E_a) of dissolution was evaluated [10,14]. The experimental results are shown in Table 9. Here, the dissolution time means a time required for the dissolution of 2.30 mg of a PS disk in 0.5 mL of a terpene at each temperature. The E_a is estimated from the slope of an Arrhenius plot of the logarithm of dissolution time versus the inverse of dissolution temperature. Limonene and its isomers have similar low E_a of ca. 20–25 kJ/mol one another. A group of the subsequent low an E_a of 25–35 kJ/mol is the acyclic terpenes except for aldehydes in Figure 5. The dissolution rate of this group is relatively fast. The E_a s of *Abies* leaf oil and *Eucalyptus* oil are 34 and 39 kJ/mol, respectively. The alcohols of terpinene-4-ol, α -terpineol, and 2-*p*-cymenol have almost 50 kJ/mol or higher of E_a . The order of E_a agrees with that of dissolving power for PS well. These results on E_a suggest that terpinene-4-ol, 2-*p*-cymenol, bornyl acetate, and α -pinene are not suitable for practical use as a solvent for PS recycling due to their long dissolution time even though they dissolve PS. To increase the dissolution rate of PS, Noguchi et al. attempted the addition of ethanol to limonene [6]. Although ethanol is not a solvent for PS, a small amount of ethanol gives the viscosity of the PS solution to lower. This method will be effective when the terpenes have a considerable

high dissolving power for PS and a high viscosity of the PS solution prevents PS from diffusing in the solution.

5. Recovery of PS and natural solvents, and physical properties of the recycled PS

Currently, it entails a high cost to gather natural solvents such as essential oils for the recycling of waste EPS, so that the recovery and reuse of the solvent are required. In addition, the properties and performance of the recycled PS are important. Terpenes and PS can be simply recovered by steam distillation of a solution of PS in terpenes; a typical example is as follows. A 10% solution of PS in geranyl acetate is subjected to steam distillation to recover 98% of the geranyl acetate used. The \bar{M}_n of the PS recovered slightly decreased from 1.2×10^5 to 1.0×10^5 , and polydispersity of the molecular weight distribution increases from 2.5 to 3.1 [10]. This means that small degradation of PS occurs during steam distillation process. However, in other petroleum-based solvents, further degradation takes place owing to the oxidative scission of PS chains by air [21]. Most terpenes have C=C groups that inhibit PS from oxidative decomposition by self-oxidation of the C=C groups. The PS recycled from limonene solutions has almost the same elastic modulus and glass transition temperature [8], indicating that it retains original mechanical properties.

6. Conclusion

The essential oil in plants and its main components, terpenes and terpenoids, are good solvent for PS. EPS is recyclable by using those natural solvents in place of petroleum-based ones. The dissolving power of terpenes for PS strongly depends on their chemical structure. Basically, terpenes of which solubility parameter is close to that of PS dissolve much PS as predicted from the theory, as well as the dissolution rate is high as that of toluene, a petroleum-based solvent. In oxygen-containing terpenes, the ethers and esters show higher dissolving power than the alcohols according to the rule of solubility parameter. However, even though the solubility parameter is close to that of PS, acyclic terpenes have higher dissolving power compared to cyclic ones and bicyclic terpenes show relatively low dissolving power and dissolution rate for PS. These findings enable the judgment whether a certain terpene is suitable for the solvent of PS recycling from the chemical structure. The PS recovered by means of steam distillation of a solution of PS in terpenes shows slightly reduced molecular weight, but almost the same mechanical properties, compared to the original PS. Such reduction of molecular weight can be minimized by steam distillation under nitrogen atmosphere. Since *Abies sachalinensis* and *Eucalyptus* species are of fast-growing and the leaf oils contain many mono-terpenes, they will be useful biomass for the solvent of PS recycling.

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