Solubilization of Polystyrene into Monoterpenes

Running Head: SOLUBILIZATION OF POLYSTYRENE INTO MONOTERPENES

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ABSTRACT: The ability of certain monoterpenes from the essential oils of *Abies sachalinensis* and *Eucalyptus* species to dissolve polystyrene (PS) was studied. These two essential oils themselves were also examined. The aim of this study is to recycle PS without a melting process and without using petroleum-derived solvents. The relationship between chemical structure of the terpenes and their dissolving power for PS was investigated through the solubility parameter and apparent activation energy for dissolution. α-Terpinene and its positional isomers on a C=C bond had high solvent powers for PS, whereas bicyclic terpenes were inferior in this regard even though they have similar solubility parameters to that of α-terpinene. It was suggested that the bulky and/or hydrophilic structures in the solvent molecule prevent the dissolution of PS. Simple steam distillation of solutions of PS in the terpenes gave recovery of more than 97 % of the PS and terpenes. The present solvent systems cause little degradation to PS and are promising for the recycling of PS using sustainable solvents.

Introduction

The recycling of resources and waste 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 should receive similar attention. Polystyrene (PS) is widely used in packaging and building materials and for electrical and thermal insulators. For the recycling of PS, melting[1] or solvent treatment[2,3] is required to reduce the volume and for subsequently reshaping the plastic. The melting process involves some chemical degradation and cannot avoid decreasing the quality of the original PS, so solvents are, 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-derived solvents are not favorable to the global environment.

d-Limonene, which is the main component of citrous oils, acts as a solvent for PS.[4,5] Lately, the recycling of PS using *d*-limonene has been realized in practical use on an industrial scale. However, except for *d*-limonene, there is no report on such other familiar natural solvents for PS as essential oils. As *d*-limonene is one of the terpenes, other monoterpenes are expected to be able to dissolve PS as well. We paid attention to the fact that the leaf oils of *Abies sachalinensis* and *Eucalyptus* species, whose growth is comparatively

fast, are biomass without much use and contain many monoterpenes. These oils and terpenes are abundant compared with *d*-limonene. This paper reports the dissolution behavior of PS into the natural solvents described above. The relationship between chemical structure of the terpenes and dissolution potential for the PS is discussed through the solubility parameter and dissolution rate. Furthermore, the recovery of PS and terpenes from the solutions obtained is mentioned from the viewpoint of PS recycling using this system.

Experimental

MATERIALS AND MEASUREMENTS

All the terpenes and *Eucalyptus* oil examined are commercially available (Tokyo Chemical Industry, Japan), and were used without any purification. *Abies* leaf oil was prepared by refluxing for 6 h in water and subsequent steam distillation of the leaves of *Abies sachalinensis*. PS was supplied from Tosoh (Japan), and labeled identifiably as XC-520. The molecular weights and their distributions of the PS before and after dissolution tests were measured by gel permeation chromatography (GPC) in chloroform referenced to standard PS samples (Product No. SM-105) (Showa Denko, Japan).

PREPARATION OF PS PIECES

The commercial PS was received in pellet form. Therefore, it was subjected to the following treatment to attain thin film prior to being dissolved. The pellets were pressed under 20 MPa at 260 °C for 5 min and then were cooled to room temperature maintaining the pressure. From the PS film obtained, circular pieces with a diameter of 5 mm were punched out. These pieces, with an average weight of 2.304 ± 0.061 mg, were adopted for the solubility test.

SOLUBILITY TEST OF PS

A piece of the PS mentioned above was put in a test tube with 0.5 mL of the terpene or oil at 30, 40, 50, 60, or 70 °C controlled by a thermostatic water bath. The tube was sealed with a silicon stopper, and shaken mechanically. Judgment of the dissolution was performed by the visual and/or polarizing microscopic observations when the piece disappeared, and the system was completely homogeneous within 24 h. The time of dissolution for the first PS piece was measured at each temperature. The next PS piece, if necessary, was added after complete dissolution was achieved. In all solubility tests, the average of five measurements with an experimental error less than 1 % was accepted for each sample.

RECOVERY OF THE PS AND TERPENE FROM THE SOLUTION

Approximately 0.2 g of the PS films was completely dissolved in 2 mL of the terpene.

After 50 mL of water was added to the solution, the mixture was subjected to steam

distillation for 3 h to be separated into solid PS and a distillate. The weight of the PS

recovered and the volume of terpene divided from the distillate were compared with those

before dissolving, respectively.

Results and Discussion

When some commercial terpenes were dropped on a block of common expanded PS, the

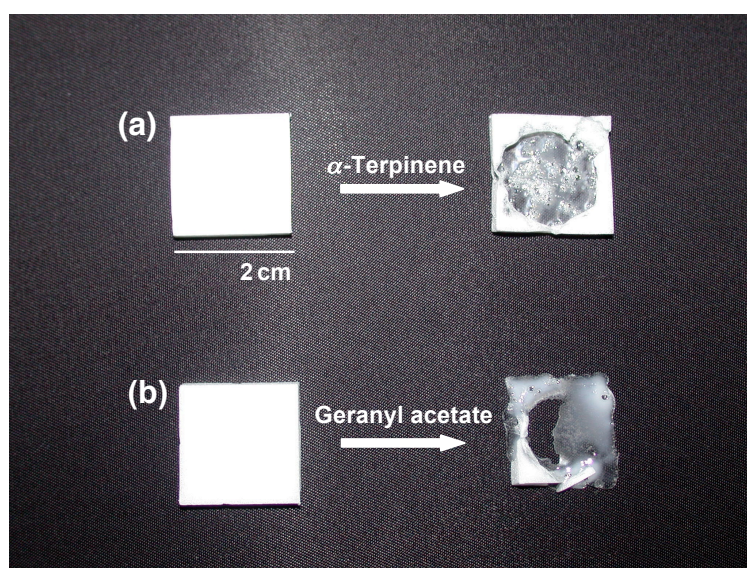PS was dissolved and shrank promptly. Figure 1 shows the appearances in the case of (a) α-

FIGURE 1. Expanded PS dissolved by (a) α-terpinene and (b) geranyl acetate.

terpinene and (b) geranyl acetate, respectively. The degree and rate of dissolution were

considerably different in each terpene. We first examined the maximum solubility of PS at

50 °C in several monoterpenes contained in the essential oils of *Abies sachalinensis*[6,7] and

Eucalyptus[8] species. It was estimated from the ratio of total weight of the PS pieces dissolved

to the weight of the terpene by converting it per 100 g of the terpene. The PS pieces were

prepared from a commercial PS pellet (number-average molecular weight; $\overline{M}_n$= 1.2 × 10^5).

The results are presented in Table I.

TABLE I. Solubility of PS in Several Terpenes and Toluene at 50 °C

Solvent	Solubility (g [100 g solvent]$^{-1}$)
α-Terpinene	130.2
γ-Terpinene	130.6
d-Limonene	126.7
Terpinolene	125.2
Geranyl acetate	174.4
Bornyl acetate	67.2
1,8-Cineole	54.8
α-Pinene	43.8
Toluene	116.9

α-Terpinene and γ-terpinene were capable of dissolving more than 130 g PS per 100 g of terpinene. The values were higher than those of d-limonene and toluene. The four terpenes from the upper row in Table I are structural isomers with different locations of a C=C bond, so they would have similar dissolving powers for the PS. Geranyl acetate showed remarkably high dissolving power for the PS of 174 g per 100 g of it. Generally, the existence of oxygen atoms in a solvent molecule prevents the solvent from interacting with PS, because PS is of low polarity consisting only hydrocarbon moieties. The reason why geranyl acetate

α-Phellandrene   Terpinolene   Geranyl acetate   γ-Terpinen

α-Terpinene   d-Limonene   α-Pinene   1,8-Cineole
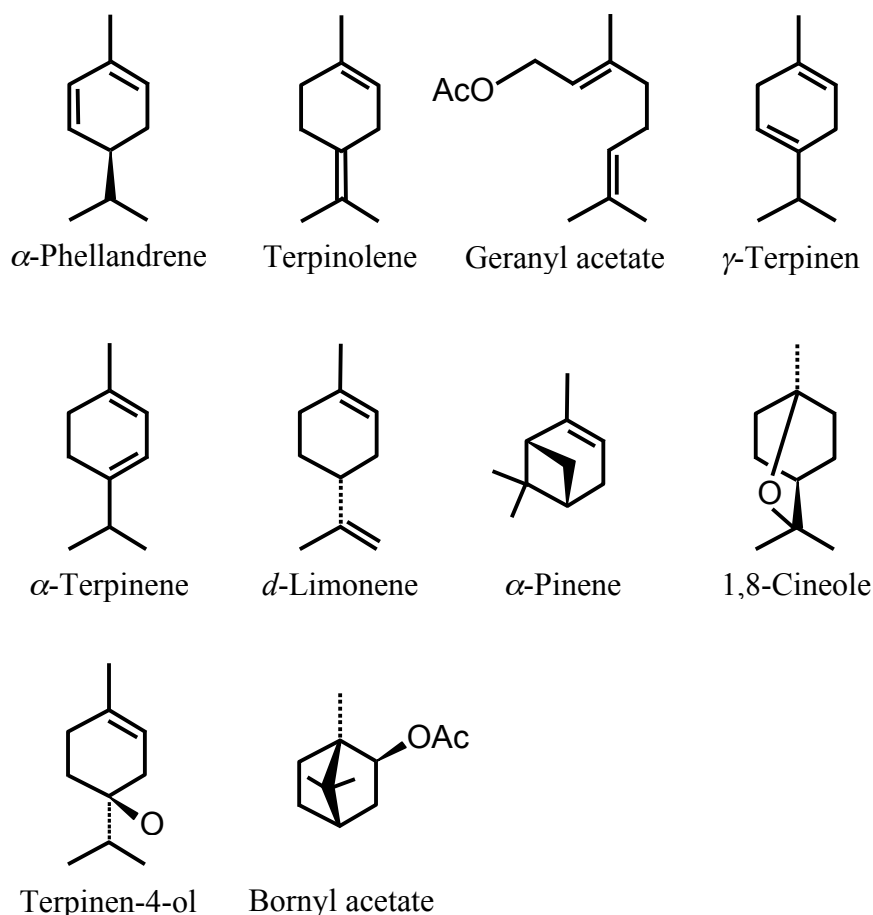
Terpinen-4-ol   Bornyl acetate

FIGURE 2. Structure of terpenes used in the dissolution of PS.

has such higher dissolution power for PS, in spite of possessing two oxygens in the molecule, is probably based on its flexible linear molecular structure, which is more accessible to the inside of bulk PS compared with cyclic terpenes. The solubilities in bornyl acetate, 1,8-cineole, and α-pinene were relatively low.

To elucidate the relationship between chemical structure of the terpenes and dissolution behavior of PS in detail, apparent activation energy (E_a) for the dissolution, and solubility parameter (δ) of the terpenes shown in Figure 2 were investigated. The δ value was calculated by the method of Hoftyzer and Van Krevelen.[9] The E_a was derived from an Arrhenius plot, using the average of five repeated measurements of the dissolution time of PS at five different temperatures. Normally, a frequency factor in the Arrhenius equation does not change dramatically depending on the temperature,[10] therefore, the E_a is an expressible index of the dissolution rate in the present system. Not only dissolving power but also dissolution rate is one of the important factors on evaluating the performance of a solvent when the recycling efficiency of PS is being considered. Referring to Table II, the order of the dissolution rate does not match completely with that of the dissolving power in Table I. However, α-terpinene and the three isomers, whose δ was very close to one another (14.88 – 15.71 $MPa^{1/2}$), had similar high dissolution rates for PS. The δ values were close to that of PS (δ_{PS}) of 14.45

TABLE II. Dissolution Time and Apparent Activation Energy (E_a) for the Dissolution of PS and Solubility Parameter (δ) of the Terpenes.

Solvent	Dissolution Time [a] (sec)					E_a (kJ mol^{-1})	δ (MPa$^{1/2}$)
	30 °C	40 °C	50 °C	60 °C	70 °C		
Terpinolene	525	425	365	301	248	16.0	15.71
Geranyl acetate	719	543	493	424	269	19.1	17.03
γ-Terpinene	496	359	289	240	196	19.7	15.15
α-Terpinene	545	401	334	262	208	20.3	14.88
d-Limonene	519	471	375	283	200	20.7	15.23
Abies leaf oil	2230	975	669	507	437	34.2	– [b]
α-Pinene	– [c]	1860	852	600	503	38.5	13.62
Eucalyptus oil	1930	785	546	448	257	39.9	– [b]
1,8-Cineole	4480	1390	626	478	302	56.3	15.04
Terpinen-4-ol	– [c]	4430	1810	950	610	59.0	19.12
Bornyl acetate	14900	3660	1590	862	558	69.8	15.92

[a]The average of five times measurements.

[b]The δ is not given because the oil is a mixture of several terpenes.

[c]Insoluble.

MPa$^{1/2}$ as well. A solute is soluble well, in general, into a solvent having close δ value to that of the solute,[11] hence, it is reasonable that the above four terpenes had high dissolution power and rate for PS. Geranyl acetate gave similar high dissolution rate, although the δ (17.03 MPa$^{1/2}$) is apart from δ_{PS}. The unexpected behavior of geranyl acetate was also observed in the experiment of dissolving power as described above. The acyclic and flexible structure of

geranyl acetate would be advantageous for access into the entangled PS molecules.

Another important finding is that the dissolution rates of α-pinene, 1,8-cineole, and bornyl acetate for PS were low even though each δ was close to δ_{PS}. This behavior is deduced from the fact that these three terpenes have a bicyclic structure, which is sterically bulky to interfere with the penetration into PS matrix. A δ is evaluated by addition and subtraction of the contribution parameters corresponding to the partial structural groups of a molecule because of the difficulty of direct measurement.[9] The three dimensional structure of a molecule is not reflected upon the δ. Thus, we concluded that bicyclic solvents do not always dissolve polymeric materials even though the δ is close to each other. The relatively low dissolution rate of the two leaf oils must be due to the components: half of *Abies* oil consists of α-pinene, camphene (solid), and bornyl acetate[6]; *Eucalyptus* oil contains ca. 30% of 1,8-cineole and 38% of α-pinene.[8] Nevertheless, these two oils also include other terpenes shown in Table II and have enough potential to be a solvent for PS recycling.

The recovery of PS and terpenes from the solutions obtained was studied through the system of geranyl acetate. Steam distillation of the 10% (w/v) of the PS solution gave a recovery of geranyl acetate of 97.6%. The $\overline{M}_n$ of the PS decreased from 1.2×10^5 to 1.0×10^5 and the molecular weight distribution increased from 2.5 to 3.1, indicating that certain

degradation occurred slightly in the PS. The occurrence of this degradation is likely to be

caused by oxygen radicals from air during the dissolving and/or recovering process.[1] To

minimize such degradation, the addition of radical scavengers to the system should be

effective.

In conclusion, some monoterpenes, particularly geranyl acetate and the isomers of

d-limonene, in the essential oils of *Abies sachalinensis* and *Eucalyptus* species dissolved PS

in high concentration. The oils themselves also dissolved PS. The PS and terpenes can be

recovered from the solutions in high yield. These findings lead to a nonpetroleum solvent for

PS and the possibility of PS recycling without a melting process.

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