Essential Oils from *Citrus reticulata* cv. Shatangju Peel: Optimization of Hydrodistillation Extraction by Response Surface Methodology and Evaluation of Their Specific Adhesive Effect to Polystyrene

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ABSTRACT: Essential oil (Eo) from the *Citrus reticulata* peel has been widely used, and its adhesive effect on polystyrene (PS) was found accidentally. To analyze the essential oils of *C. reticulata* cv. Shatangju (CrspEos), the extraction of these oils by steam distillation was optimized using the response surface method. The chemical composition of CrspEos was analyzed by gas chromatography−mass spectrometry. Then, the adhesive effect of these essential oils on PS was evaluated. The adhesion area, the influence of adhesion on the thickness of the essential oil on the materials, the effect of adhesion on the transmittance of PS, the strength of adhesion point, and specificity of adhesion were determined. The optimum extraction conditions resulting in the extraction yield of 47.37 μL g^{-1} were a ratio of liquid-to-solid of 8.94:1, a soaking time of 199.45 min, and an extraction time of 138.71 min. The major component in the essential oils was D-limonene (56.66%), followed by myrcene (6.62%). CrspEos presented a specific adherence effect on PS without influencing the thickness and transmittance of PS but with stronger tenacity than the parent material. CrspEos can be used as an environmentally friendly specific adhesive for PS.
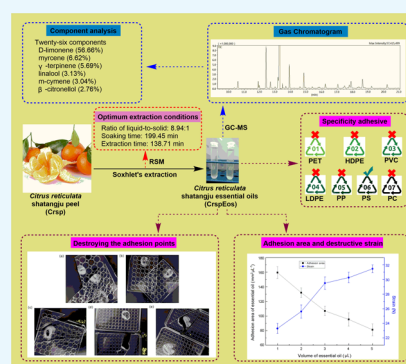
1. INTRODUCTION

Polystyrene (PS) has excellent optical properties, with a transmittance of 88−92% and a refractive index of 1.59−1.60. This polymer can pass through all wavelengths of visible light. PS is easy to process and form, transparent, inexpensive, rigid, insulative, and good printing applications. This material is widely used as optical chemical instrument parts in lighting instruction, lampshades in daily decoration, a transparent film in packaging, and various meter shell and capacitor dielectric layer in the electrical appliance industry.[1−3] Similar to other plastic products, damaged PS products can be repaired using an adhesive.

Adhesives are derived from synthetic and natural resources, but synthetic adhesives still dominate this market. The preference for more environmentally friendly, naturally derived materials is driven by the strict government regulations to reduce and even eliminate materials that are slightly toxic and enhance consumer awareness. The majority of reported natural adhesives are for wood and cellulose, including tannin, lignin, protein, carbohydrate, and unsaturated oil. Only two seed oil derivatives have been translated recently as wood adhesives. For example, linseed oil has been applied to prepare a resin that can be used as an adhesive or surface-coating material.[4,5] No naturally derived adhesive but two specific synthetic adhesives have been reported for PS. One adhesive contains isoamyl acetate, chloroform, acetone, polystyrene waste (w/w/w/w, 60:13:20:7), while the other type consists of poly-ethylene (high boiling substance at 40−60 °C), isooctyl acetate, chloroform, and polystyrene (w/w/w/w, 50:20:13:7).[6]

The essential oils (Eos) in orange peel have various activities with an orange flavor. These Eos are colorless or slightly yellow and account for 1.06−4.62% of the total weight of the dry peel.[7] The extraction, chemical composition, and biological activity of the Eos from *Citrus reticulata* Blanco and *Fortunella margarita* (Lour.) Swingle peels have been reported. Liu et al.[8] optimized the extraction of Eos using response surface methodology (RSM). The results showed an oil yield of 2.14% in a liquid-to-material ratio of 8.4:1 (mL g^{-1}), sodium chloride concentration of 5.3%, and distillation time of 3.5 h. A total of 39 different components had been identified by gas chromatography−mass spectrometry (GC−MS) analysis.[8] With the use of CO$_2$ supercritical fluid extraction, Mira et al. found that temperature and pressure could affect the Eos composition.[9] Hosni analyzed the components of the products from four types of citrus peels, and the results showed that monoterpenoid hydrocarbons accounted for 97.59−99.3%, which included 92.52−97.3% of limonene and 1.37−1.82% of β-pinene.[7] Wang reported that the Eos from orange peel can
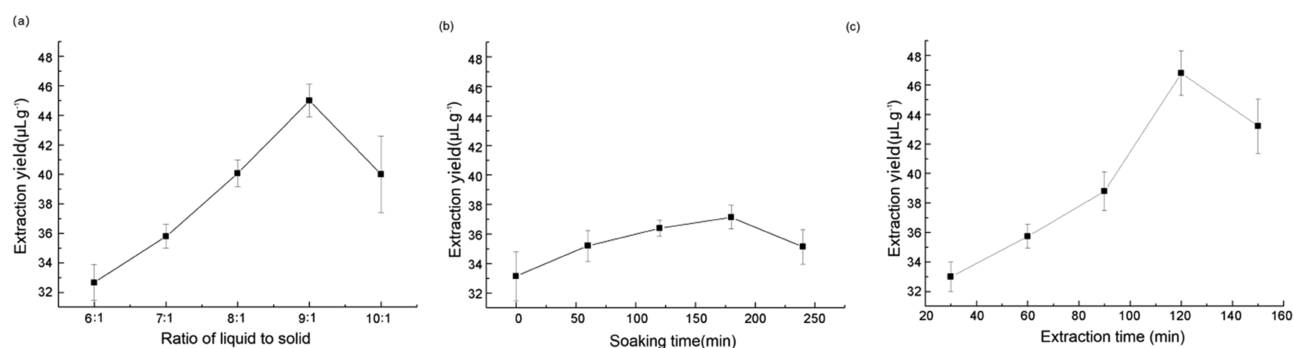
Figure 1. Effects of different factors on the extraction of CrspEos: (a) liquid-to-solid ratio; (b) soaking time (min); and (c) extraction time (min). Data are shown as mean ± standard deviation (SD) ($n = 3$).

be used to recover expanded PS (EPS).[10] Limonene, which is a component of citrus Eos, is a pioneer of natural solvents for EPS.[11−13] D-Limonene, with the function of recycling PS, is used to prepare nanocomposite polymers. This component is also used as a monomer that undergoes UV-catalyzed thiol-ene polymerization reactions with polythiol comonomers to produce polymeric products consisting of precipitated PS phases dispersed throughout the elastomeric poly (thioether) networks.[14]

The Eos from the peel of *C. reticulata* cv. Shatangju (Crsp) is rarely reported. In this study, the response surface method was used to optimize the extraction of the Eos from Crsp (CrspEos) by steam distillation. The chemical composition and amount of CrspEos were analyzed by gas chromatography−mass spectrometry (GC−MS). The adhesive effect of CrspEos on PS was also evaluated.

2. RESULTS AND DISCUSSION

2.1. Single-Factor Experiment. The ratio of liquid-to-solid, soaking time, and extraction time were selected as targets in the single-factor experiments. The other variables were controlled, and the effects of each factor on the extraction of CrspEos were determined.

With the ratio of liquid-to-solid of 6:1−10:1, soaking time of 0 min, and the extraction time of 60 min, it was found that as the ratio of liquid-to-solid increased, the yield of Eos increased gradually, reached 45.00 ± 1.11 μL g^{-1} at 9:1, and then decreased (Figure 1a). Therefore, the optimum ratio of liquid-to-solid was set as 9:1.

Soaking time was also an influencing factor in the extraction of Eos. Figure 1b shows the results when the ratio of liquid-to-solid and extraction time were controlled at 7:1 and 60 min, respectively; therefore the soaking time was set in the range of 0−240 min. The extraction yield of CrspEos ($Y_{CrspEos}$) significantly increased to 37.81 ± 0.81 μL g^{-1} when the soaking time was increased from 0 to 180 min but decreased from 180 to 240 min.

Different extraction times were set to 30, 60, 90, 120, and 150 min with the ratio of liquid-to-solid of 7:1 and the soaking time of 0 min. $Y_{CrspEos}$ was enhanced obviously to 46.80 ± 1.51 μL g^{-1} within the extraction time range of 30−120 min and then decreased (Figure 1c).

2.2. RSM Analysis. The designed and experimental data of the ratio of liquid-to-solid (X_1), soaking time (X_2), and extraction time (X_3) are shown in Table 1. The 20 experimental runs, including 8 (2^3) factor points, 6 extra points (star points), and 6 center points, are also listed in Table 1. Six replicates of the center point were used to evaluate

Table 1. Central Composite Design Matrix of the Three Variables—Liquid-to-Solid Ratio (X_1), Soaking Time (X_2), and Extraction Time (X_3)—for the Extraction of CrspEos

				extraction yield (μL g^{-1})	
no.	$X_1{}^{aR}$	$X_2{}^{bS}$	$X_3{}^{cE}$	predicted	experimental
1	−1	1	1	45.85	46.00
2	−1	1	−1	40.06	40.67
3	−1	−1	1	38.87	39.33
4	−1	−1	−1	36.58	36.67
5	1	1	1	42.70	43.33
6	1	1	−1	40.75	41.00
7	1	−1	1	41.55	41.67
8	1	−1	−1	43.09	43.67
9	1.682	0	0	43.26	42.67
10	−1.682	0	0	40.43	40.00
11	0	1.682	0	40.96	40.33
12	0	−1.682	0	37.06	36.67
13	0	0	1.682	45.46	45.00
14	0	0	−1.682	41.89	41.33
15	0	0	0	46.86	46.67
16	0	0	0	46.86	46.33
17	0	0	0	46.86	46.67
18	0	0	0	46.86	47.00
19	0	0	0	46.86	47.67
20	0	0	0	46.86	47.00

^{aR}atio of liquid-to-solid (mL g^{-1}); the five levels (−1.682, −1, 0, 1, 1.682) correspond to 7.32:1, 8:1, 9:1, 10:1, and 10.68:1, respectively. ^{bS}oaking time (min); the five levels (−1.682, −1, 0, 1, 1.682) correspond to 79.09, 120, 180, 240, and 280.91, respectively. ^{cE}xtraction time (min); the five levels (−1.682, −1, 0, 1, 1.682) correspond to 69.55, 90, 120, 150, and 170.45, respectively.

the experimental errors and the repeatability of the calculation method.[15] The quadratic polynomial regression model of the three factors was generated as follows

$$Y = -218.5449 + 40.98538X_1 + 0.45761X_2 + 0.53568X_3$$
$$- 0.024333X_1X_2 - 0.031917X_1X_3 + 4.86111$$
$$\times 10^{-4}X_2X_3 - 1.77411 \times 10^{-3}X_1^2 - 7.71232$$
$$\times 10^{-4}X_2^2 - 1.25234 \times 10^{-3}X_3^2$$

where Y is the yield of CrspEos (μL g^{-1}), and X_1, X_2, and X_3 are the coded variables for the ratio of liquid-to-solid, soaking time, and extraction time, respectively.

The findings from the analysis of variance (ANOVA) of the experimental results are shown in Table 2. The values of F

Table 2. Variance Analysis of the Extracted Equation of CrspEos

source	sum of squares	df	mean square	F value	P-value prob > F	
model	225.1686	9	25.01873	61.7612	<0.0001	significant
X_1	9.667599	1	9.667599	23.86542	0.0006	
X_2	18.31503	1	18.31503	45.21245	<0.0001	
X_3	15.3786	1	15.3786	37.96358	0.0001	
X_1X_2	17.0528	1	17.0528	42.09651	<0.0001	
X_1X_3	7.33445	1	7.33445	18.10581	0.0017	
X_2X_3	6.125	1	6.125	15.12016	0.0030	
X_1^2	45.35916	1	45.35916	111.9735	<0.0001	
X_2^2	111.0908	1	111.0908	274.2386	<0.0001	
X_3^2	18.30775	1	18.30775	45.19448	<0.0001	
residual	4.050882	10	0.405088			
lack of fit	3.007882	5	0.601576	2.883875	0.1349	not significant
pure error	1.043	5	0.2086			
cor total	229.2195	19				
R^2	0.982327					
adj R^2	0.966422					
pred R^2	0.891967					
adeq precision	22.8436	C·V%	1.48			

(61.76) and $P < 0.0001$ indicated that the quadratic regression equation was ideal, and the model was highly significant. The linear coefficients (X_1, X_2, and X_3), interaction coefficients (X_1X_2, X_1X_3, and X_2X_3), and quadratic coefficients (X_1^2, X_2^2, and X_3^2) had significant effects ($P < 0.01$). The influence of the conditions on the CrspEos yield followed the order of soaking time (X_2, min), extraction time (X_3, min), and the ratio of liquid-to-solid (X_1). The P-value of the lack of fit was 0.1349 (>0.05), indicating that the experimental data adapted to the model.

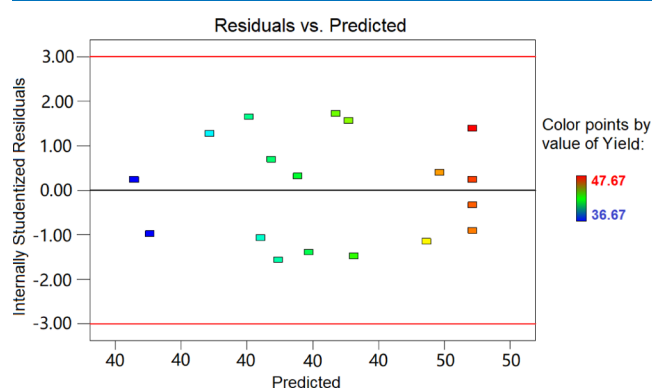The residual-standard values in Figure 2 were all in ±3 intervals, suggesting that the model was consistent with the

Figure 2. Studentized residuals and the predicted response plot.

experimental data with no error recorded.[16] The adequate precision was 22.8436, which is more than 4, indicating an adequate signal and the suitability of this model to be applied in the navigation-design space. Thus, this model can be used to navigate the design space. The "Pred R-Squared" of 0.8920 reasonably agreed with the "Adj R-Squared" of 0.9664. The two values indicated the total variability of the model response, and the determined value of the coefficient indicated the model accuracy.

Figure 3 shows the response surface (three-dimensional (3D)) for $Y_{CrspEos}$ as a function of various ratios of liquid-to-solid and soaking times at a fixed extraction time of 138.73 min. $Y_{CrspEos}$ increased rapidly when the ratio of liquid-to-solid

was increased from 8 to 9 but decreased rapidly when the ratio of liquid-to-solid increased beyond 9. Moreover, $Y_{CrspEos}$ increased with increased soaking time from 120 to 210 min and then decreased from 210 to 240 min. In theory, soaking can lead to the expansion of the tissue cells and enlargement of the intercellular space. The phenomena accelerate the dynamic exchange of the internal and external liquids of the cells and facilitate the extraction of the Eos.[17] When the soaking time is too long, pectin and other components in the raw materials will be dissolved, resulting in the emulsifying effect, thereby inhibiting the distillation of Eos. These events will lead to a decrease in the oil yield.[18] The 3D response surface plots in Figure 4 show the effects of the ratio of liquid-to-solid and the extraction time. It was found that $Y_{CrspEos}$ improved first with the increase of the ratio of liquid-to-solid from 8 to 9 or the extraction time from 90 to 138 min, but did not increase significantly with further increase in either parameter. Increasing the ratio of liquid-to-solid is favorable for the diffusion and dissolution of the Eos, and the mass transfer rate also increases. When the ratio of liquid-to-solid is too high, the heating time will be longer and the amount of Eos generated at the same time will be reduced, and energy will be wasted.[19] Increasing the soaking time or extraction time enhanced $Y_{CrspEos}$ in the initial stage of the reaction (Figure 5). According to Ahmed, further increase in the extraction time increases the oil yield, but the oil quality deteriorates beyond 3 h.[20] The optimized conditions for the experiment were the ratio of liquid-to-solid of 8.94, soaking time of 199.49 min, and extraction time of 138.76 min. An additional run was conducted to evaluate the accuracy of the model. Under the optimized extraction conditions, the predicted and actual values (mean of three measurements) of the Eos yield were 47.35 and 47.37 $\mu L\ g^{-1}$, respectively. The agreement between the predicted and actual values indicated that the model was adequate for the extraction process.

2.3. Eos Yield and Characterization. As shown in Figure S1, the components of CrspEos were analyzed by GC−MS, and 26 components were identified. The Eos mostly consisted of terpenoid and aldehyde groups, including D-limonene (56.66%), myrcene (6.62%), γ-terpinene (5.69%), linalool (3.13%), m-cymene (3.04%), and β-citronellol (2.76%). These
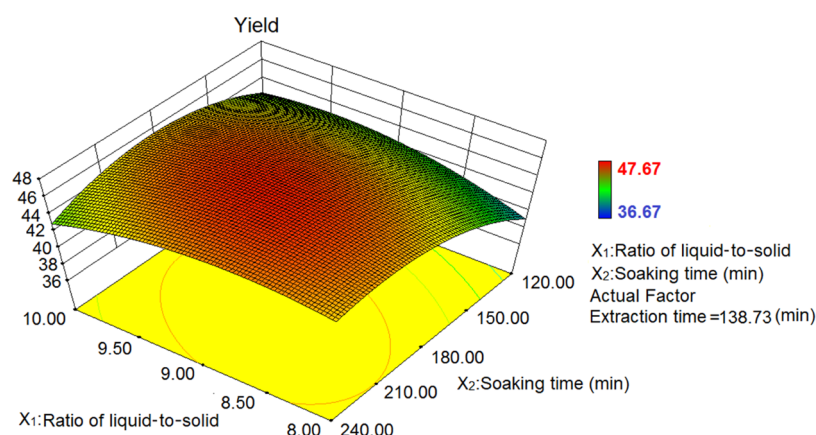
Figure 3. Response surface (3D) showing the effects of the ratio of liquid-to-solid vs soaking time (min) on the yield of CrspEos.
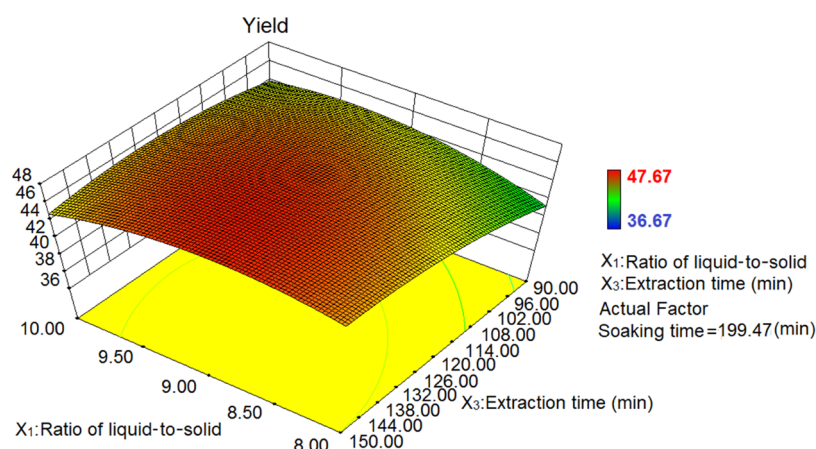

Figure 4. Response surface (3D) showing the effects of the ratio of liquid-to-solid vs extraction time (min) on the yield of CrspEos.
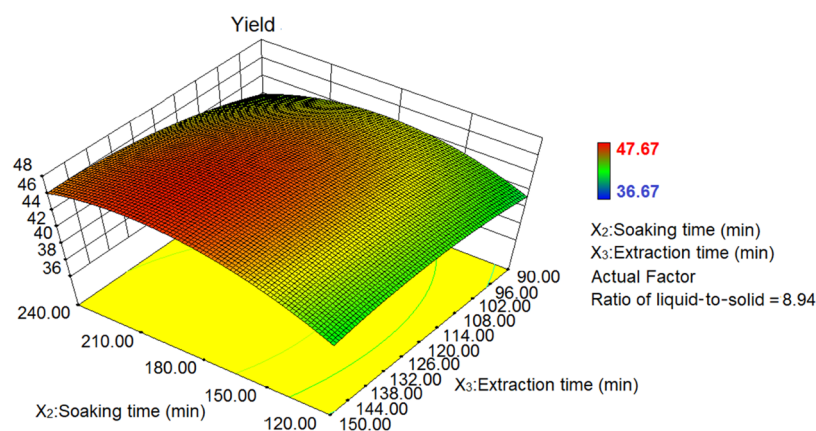

Figure 5. Response surface (3D) showing the effects of soaking time (min) vs extraction time (min) on the yield of CrspEos.

six components accounted for 78.1% of the total Eos (Table 3). The chemical constituents of the Eos from the orange peel were analyzed by GC−MS. The terpenoid and aldehyde groups were the main components of the Eos from the orange peel, but other components varied slightly.[8,21] This result may be due to the fact that the oranges used were obtained from different places and production seasons.

2.4. Adhesive Effect of CrspEos on PS. The adhesive effect of CrspEos on PS was discovered accidentally during an experiment when the CrspEos was dropped on the surface of the PS cover of 96-well plates (the smooth surface). To

investigate in detail the adhesive effect, the adhesion area of the Eos, influence of adhesion on the thickness of the Eos on the materials, effect of adhesion on the transmittance of PS, strength of adhesion point, and specificity of CrspEos adhesion were measured.

As shown in Figure 6, the adhesion area was decreased from 159.51 ± 8.03 to 81.12 ± 8.13 mm^2 μL^{-1} Eos with increasing volume of the Eos from 1 to 5 μL. The strain increased from 23.29 ± 0.68 to 31.46 ± 0.53 N, and the larger adhesion of the joint was accompanied with more adhesion strength. The CrspEos could adhere to PS by dissolving. This process can be

Table 3. Relative Percentage Composition of CrspEos

no.	compounds	RI^{aR}	molecular formula	area (%)
1	α-thujene	924	$C_{10}H_{16}$	0.13
2	(+)-α-pinene	948	$C_{10}H_{16}$	1.41
3	sabinene	984	$C_{10}H_{16}$	1.07
4	β-pinene	985	$C_{10}H_{16}$	0.47
5	myrcene	993	$C_{10}H_{16}$	6.62
6	octanal	995	$C_8H_{16}O$	1.85
7	α-terpinene	998	$C_{10}H_{16}$	0.67
8	m-cymene	1025	$C_{10}H_{14}$	3.04
9	D-limonene	1028	$C_{10}H_{16}$	56.66
10	nd	1033	ND	0.41
11	β-cis-ocimene	1040	$C_{10}H_{16}$	0.77
12	γ-terpinene	1056	$C_{10}H_{16}$	5.69
13	terpinolene	1083	$C_{10}H_{16}$	0.99
14	linalool	1090	$C_{10}H_{18}O$	3.13
15	1-nonanal	1095	$C_9H_{18}O$	0.67
16	β-terpineol	1123	$C_{10}H_{18}O$	0.92
17	citronellal	1125	$C_{10}H_{18}O$	1.57
18	terpinen-4-ol	1170	$C_{10}H_{18}O$	1.55
19	α-terpineol	1175	$C_{10}H_{18}O$	1.55
20	dihydrocarveol	1177	$C_{10}H_{18}O$	0.50
21	trans-carveol	1189	$C_{10}H_{16}O$	1.27
22	decanal	1192	$C_{10}H_{20}O$	2.20
23	1-p-menthen-9-al	1217	$C_{10}H_{16}O$	0.46
24	lemonol	1221	$C_{10}H_{18}O$	0.94
25	β-citronellol	1231	$C_{10}H_{20}O$	2.76
26	L(-)-carvone	1254	$C_{10}H_{14}O$	1.06
27	perillaldehyde	1255	$C_{10}H_{14}O$	1.65

^{aR}retention indices determined on the Rxi-5 column, using the homologous series of n-alkanes (C_8–C_{14}). ^{b}nd: not determined.
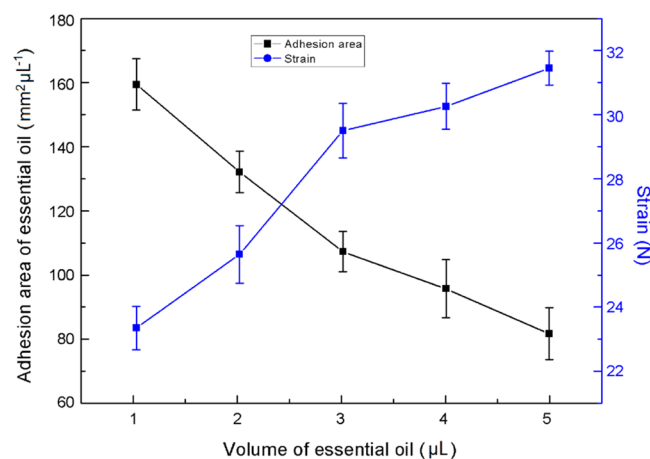

Figure 6. Relationship of adhesion area of CrspEos, the strain for destroying the adhesion points, and the volume of CrspEos.

regarded as immersional wetting in interface chemistry. The surface Gibbs function (ΔG) represents the driving force of the immersional wetting process. A smaller value of ΔG indicates an easier increase in the immersional wetting area. The contact angle θ increased with the enhancement of the liquid volume, and the diminished value of cos θ led to an increase in ΔG. Thus, the adhesion point per unit volume was reduced. Second, the CrspEos dissolved in the PS increased the viscosity, and the poor fluidity reduced the adhesion area per unit volume.[22] With the increase of the volume of CrspEos, the total adhesion area increased, the bonding area became

stronger, and the damage of strain increased. The adhesion point was equivalent or had more strength than the parent material as the joint was all destroyed outside the adhesion point by the strain, which illustrated that the strength was sufficient. Some cloudiness was observed at the adhesion point after it was destroyed by external forces (Figure 7).

To evaluate the influence of adhesion on the thickness of the Eos, the adhesive failure and the change in the thickness were measured. The data can be used as a reference value to ensure the adhesion affect and avoid the squeeze-out effect. The change in the thickness on the PS before and after adhesion is shown in Table 4. The thickness was not influenced after adhesion with 1, 2, 3, 4, and 5 μL of CrspEos. The thickness of $t_{A1} + t_{A2}$ was consistent with that of $t_{A1:A2}$ ($P > 0.05$). Although, visual damage was observed at the interface between the Eos and PS, no significant difference was found in the material thickness before and after adhesion. Table 5 shows the transmittance of visible light (wavelengths in the range of 400−800 nm) through the PS material before and after adhesion. T_3 was indistinguishable from the theoretical value T_2. This phenomenon indicated that the transmittance was not influenced by the adhesive effect ($P > 0.01$).

The adhesion of CrspEos on the different plastic materials, including poly(ethylene terephthalate) (PET), high-density polyethylene (HDPE), poly(vinyl chloride) (PVC), low-density polyethylene (LDPE), polypropylene (PP), PS, and polycarbonates (PC), were investigated. The adhesion effect presented only in the group of PS/PS illustrated that CrspEos could specifically adhere to PS. The structures of the main components in CrspEos and the precursor of PS, and phenylethylene are shown in Figure 8. The similar structure may have caused the specificity of CrspEos adhesion. Hattori et al. found that D-limonene, myrcene, γ-terpinene, and m-cymene have dissolving power of nearly 127, 101, 130, and 212 g for PS per 100 g of the component, respectively.[23] Wang et al. reported that Eos from the orange peel can be used to recover the PS foam.[10]

Given that PS is prone to turbidity and yellowing because of the influence of light or dust, adding appropriate antioxidants as anti-aging agents when preparing optical components of PS is necessary.[24] CrspEos has been reported to exhibit excellent antioxidant activities.[21] The reported PS adhesives contained different proportions of restricted chemical compositions. For example, acetone (category III) is listed in the Catalogue of Precursor Chemicals in the United Nations Convention against Illicit Traffic in Narcotic Drugs and Psychotropic Substances,[25] and trichloromethane (category II) is listed in the Catalogue of Precursor Chemicals in the Regulations for the Administration of Precursors and Chemicals used in the Production of Narcotic Drugs and Psychotropic Substances.[26] In this paper, the adhesive effect of CrspEos on PS has no effect on the thickness, transmittance, and specific adhesion, indicating that the plant-derived CrspEos can be used as a candidate of environmentally friendly specific adhesive for PS with potential as an anti-aging agent. According to GB/T 2943-2008, CrspEos can be classified as a vegetable glue.[27]

3. MATERIALS AND METHODS

3.1. Materials and Reagents. C. reticulate cv. Shatangju, which was produced in Shatangkeng Village Guangxi, was purchased from the campus supermarket and identified by the Department of Pharmacy, School of Pharmacy, Jilin University. The Crsp was dried in the shade for one week at room
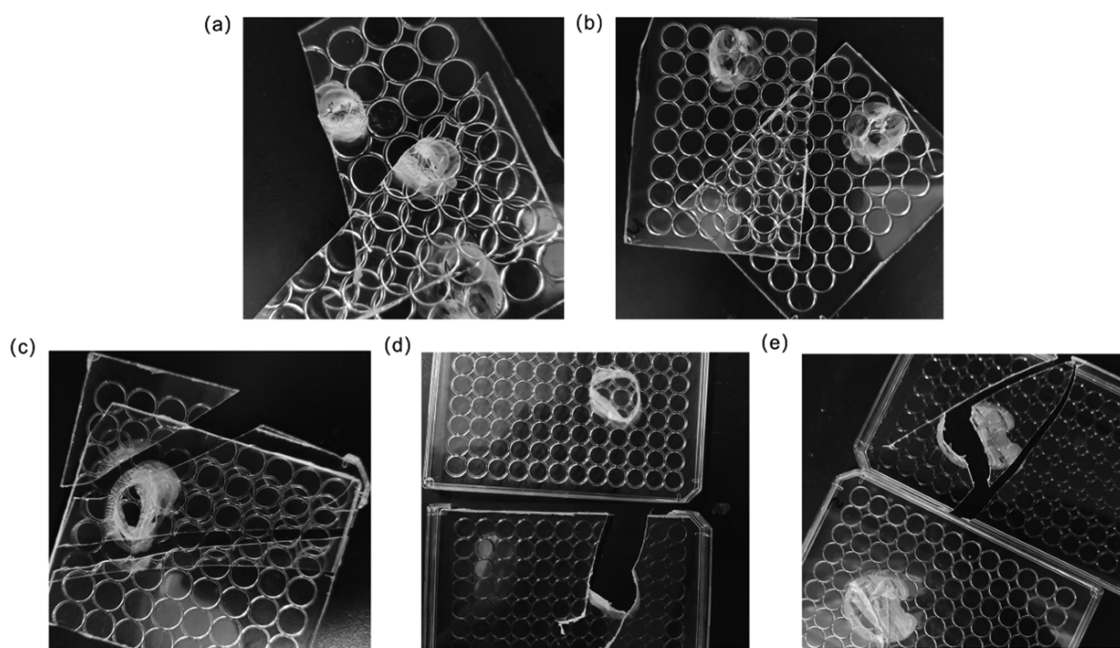
Figure 7. Damage of polystyrene adhesion points with different volumes of CrspEos by the strain. The adhesion point was adhered by (a) 1 μL of CrspEos; (b) 2 μL of CrspEos; (c) 3 μL of CrspEos; (d) 4 μL of CrspEos; and (e) 5 μL of CrspEos.

Table 4. Thickness of PS before and after Adhesion[a]

CrspEos (μL)	$t_{A1} + t_{A2}$ (mm)	$t_{A1:A2}$ (mm)	P = 0.37
1	2.42 ± 0.12	2.46 ± 0.12	P = 0.69
2	2.35 ± 0.22	2.43 ± 0.19	P = 0.66
3	2.33 ± 0.24	2.31 ± 0.27	P = 0.93
4	2.39 ± 0.18	2.33 ± 0.16	P = 0.75
5	2.38 ± 0.31	2.36 ± 0.24	P = 0.58

[a]The P-value represented the difference of the thickness of PS before and after adhesion; when $P > 0.05$, the difference was not statistically significant. t is the thickness of the PS material (A1, A2, and A1:A2).

Table 5. Transmittance (T) of PS before and after Adhesion

wavelength (nm)	T_1	T_2	T_3
400	90.77 ± 1.31[b]	82.40 ± 2.36[b]	82.83 ± 2.65[b]
420	91.73 ± 1.29[b]	84.16 ± 2.36[b]	84.40 ± 2.59[b]
440	92.17 ± 1.31[b]	84.96 ± 2.40[b]	85.37 ± 2.71[b]
460	92.90 ± 1.28[b]	86.31 ± 2.37[b]	86.43 ± 2.63[b]
480	93.00 ± 1.32[b]	86.50 ± 2.45[b]	86.77 ± 2.42[b]
500	93.00 ± 1.35[b]	86.50 ± 2.50[b]	86.87 ± 2.59[b]
520	93.03 ± 1.29[b]	86.56 ± 2.39[b]	87.13 ± 2.44[b]
540	93.03 ± 1.36[b]	86.56 ± 2.52[b]	87.30 ± 2.31[b]
560	92.93 ± 1.34[b]	86.38 ± 2.49[b]	87.47 ± 2.25[b]
580	92.87 ± 1.45[b]	86.26 ± 2.68[b]	87.77 ± 2.25[b]
600	92.97 ± 1.62[b]	86.45 ± 2.99[b]	88.17 ± 2.27[b]
620	92.97 ± 1.71[bc]	86.45 ± 3.16[b]	88.57 ± 2.35[bc]
640	93.10 ± 1.74[bc]	86.70 ± 3.23[b]	88.93 ± 2.39[bc]
660	92.67 ± 2.32[bc]	85.91 ± 4.28[b]	89.43 ± 2.29[bc]
680	92.47 ± 2.28[bc]	85.54 ± 4.20[b]	89.27 ± 2.18[bc]
700	92.90 ± 2.19[bc]	86.34 ± 4.06[b]	89.63 ± 2.03[bc]
720	93.67 ± 2.12[bc]	87.76 ± 3.96[b]	90.30 ± 1.97[bc]
740	95.40 ± 2.04[b]	91.04 ± 3.88[b]	92.03 ± 1.96[b]
760	95.70 ± 1.95[b]	91.61 ± 3.71[b]	92.23 ± 2.03[b]
780	95.60 ± 1.93[b]	91.42 ± 3.67[b]	92.10 ± 2.07[b]
800	95.33 ± 1.86[b]	90.91 ± 3.52[b]	91.90 ± 2.07[b]

[a]T_1 is the transmittance of A; T_2 is the theoretical transmittance of the $A_1:A_2$; theoretical value was calculated based on the value of transmittance of PS according to the Lambert–Beer law, and T_3 is the transmittance of the $A_1:A_2$. [b]Means in the same row with different superscript lowercase letters differ significantly ($P < 0.05$).

temperature and smashed with a medicinal pulverizer (particle size, <0.5 mm). All reagents and solvents were of analytical grade. The plastic materials for adhering included poly(ethylene terephthalate) (PET), high-density polyethylene (HDPE), poly(vinyl chloride) (PVC), low-density polyethylene (LDPE), polypropylene (PP), PS, and polycarbonates (PCs).

3.2. Experimental Design. The ratio of liquid-to-solid (X_1), soaking time (X_2, min), and extraction time (X_3, min) were selected as single factors to investigate their effects on the extraction yield of CrspEos. The three factors were assumed to be independent of each other. The Eos from dried Crsp (30 g) were extracted by hydrodistillation using a Clevenger-type apparatus. The experimental conditions are listed in Table 6. CsrpEos were collected and stored in the dark at 4 °C. The yield was calculated as follows

$$Y_{(v/w)} = V_{Eos}\ (\mu L)/W_{Crsp}\ (g)$$

where $Y_{(v/w)}$, V_{Eos}, and W_{Crsp} are the Eos yield (v/w, μL g^{-1}), the volume of Eos (μL), and the weight of Csrp (g), respectively.

Based on the single-factor experiment and according to the central composite design experimental principle,[28] a series of Eos extraction experiments was designed using 30 g of Crsp. A response surface analysis with a three-factor–five-level scheme

was formulated using Design Expert 8.0.6.1 (Stat-Ease, Inc, Minneapolis) based on the response of the CrspEos. The independent variables were coded at five levels (−1.682, −1, 0, 1, 1.682). The generalized second-order polynomial model used in the response surface analysis is as follows
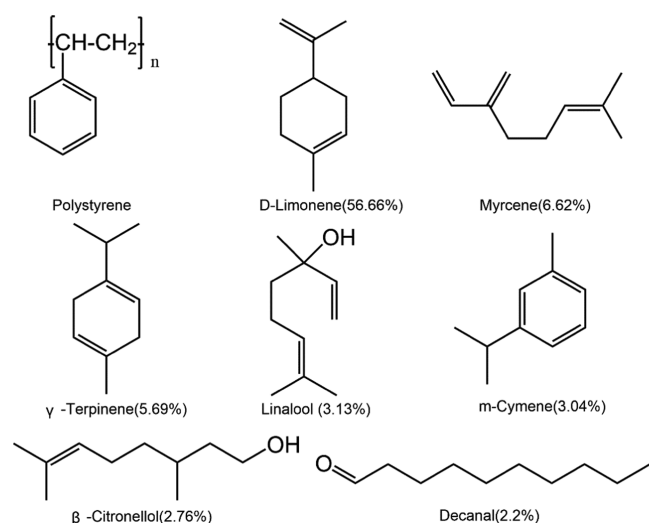
Figure 8. Structure of polystyrene and the main components of CrspEos.

Table 6. Extraction Conditions of the Single-Element Test

	ratio of liquid-to-solid	soaking time (min)	extraction time (min)
series 1	6:1, 7:1, 8:1, 9:1, 10:1	0	60
series 2	7:1	0, 60, 120, 180, 240	60
series 3	7:1	0	30, 60, 90, 120, 150

$$Y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_{11}X_1^2 + B_{22}X_2^2$$
$$+ B_{33}X_3^2 + B_{12}X_1X_2 + B_{13}X_1X_3 + B_{23}X_2X_3$$

where Y is the experimental response (yield of CrspEos); B_0 is a constant; B_1, B_2, and B_3 are the linear regression coefficients; B_{11}, B_{22}, and B_{33} are the quadratic regression coefficients; B_{12}, B_{13}, and B_{23} are the interactive regression coefficients of the model; and X_1, X_2, and X_3 are the noncoded values for the ratio of liquid-to-solid, soaking time, and extraction time, respectively

3.3. Determination of the Chemical Composition of the Eos by GC−MS. GC−MS was performed as previously reported.[29] A GC−MS instrument (Shimadzu GCMS-QP-2010 plus) was employed with the following conditions: Rxi-5MS, 30 m × 0.25 mm × 0.25 μm; helium (99.999%), carrier gas; and flow rate, 1.0 mL min^{-1}. The heating program was set to column temperature at 50 °C (held for 3 min), increased to 100 °C at 50 °C min^{-1} to 200 °C at 8 °C min^{-1} and to 290 °C at 100 °C min^{-1}, which was maintained for 10 min. The temperatures of the injector and the interface were 280 and 230 °C, respectively, and the pressure was 117.6 kPa. The Eos components were determined by comparing the Kovats index and mass spectra of known components in the mass spectrometry database (NIST).[30] The relative amount of the compounds was computed from the flame ionization detector (FID) peak areas without applying the FID response factor correction. This value was expressed as a percentage.

3.4. Adhesive Effect of CrspEos on PS. Two PS material plates (12.5 cm × 8.5 cm, A_1 and A_2) were squeezed together for 5 min after the addition of 1−5 μL of Eos between them. Adhesion was as soft as possible to prevent bubbles between the two PS plates. The adhesion plate (A_1:A_2) was used to measure the adhesion area of the Eos, the influence of adhesion on the thickness of the Eos on the materials, the effect of adhesion on light transmittance, the strength of adhesion point, and the specificity of the Eos adhesion.

3.4.1. Calculation of Adhesion Area of the Eos. The adhesion area (S) formed by the CrspEos on the PS material plates was summed depending on the area of the circle (S_1) and the middle figure of four circles (S_2) on the PS material. The area of the different volumes of Eos was calculated as follows

$$S = n_1S_1 + n_2S_2$$

$$S_1 = \pi d^2/4$$

$$S_2 = d^2 - \pi d^2/4$$

where S is the adhesion area of the Eos; d is the diameter of the circle of the 96-well plates; S_1 is the area of the circle; S_2 is the area between the four circles; and n_1 and n_2 are the numbers of S_1 and S_2, respectively.

3.4.2. Influence of Adhesion on the Thickness of Eos on the Materials. The thickness (t) values of the two PS materials (t_{A1} and t_{A2}) were measured using a Vernier caliper, and then the values were added. After adhesion, the thickness of the PS materials ($t_{A1:A2}$) was measured. Five points on the material were randomly selected for measurements. The differences between the values of $t_{A1}+t_{A2}$ and $t_{A1:A2}$ were analyzed.

3.4.3. Effect of Adhesion on the Transmittance of PS. The transmittance, which follows the Lambert−Beer law, every 20 nm in the visible-light region (400−800 nm) of A_1, A_2, and A_1:A_2 was measured using a spectrophotometer. The transmittance was calculated as follows

$$T_1 = 10^{-ECl}$$

$$T_2 = 10^{-EC2l} = T_1^2$$

where T_1 is the transmittance of A; T_2 is the transmittance of the A_1:A_2; E is the absorptivity; C is the concentration; and l is the thickness of the PS material.

3.4.4. Strength of Adhesion. The strength of the A_1:A_2 joints was evaluated according the methods of GB/T2791-1995[31] and GB/T2790-1995[32] with slight modifications. Distilled water (v) was added into a beaker (with known weight, m_0), which was connected to A of A_1:A_2, until the connecting part A_2 was separated from A_1. The strain (F) that could be endured by the A_1:A_2 joints was calculated as follows

$$F = (m_0 + v \times \rho)g$$

where v and m_0 represent the volume of the distilled water when the A_1:A_2 joint was separated and the weight of beaker, respectively; ρ is the density of the distilled water; and g is the gravitational acceleration.

3.4.5. Specificity of the Adhesion of CrspEos. To investigate the specificity of the adhesion of CrspEos on PS, six kinds of common plastic materials, namely, PET, HDPE, PVC, LDPE, PP, and PCs, were employed to replace PS.

3.5. Statistical Analysis. Adhesion experiments were performed in triplicate. The results were expressed as mean ± standard deviation. The experimental data were statistically tested by ANOVA by performing Duncan's multiple-range tests. SPSS statistical software version 19.0 was used, and $P <$ 0.05 indicated that the effect was significant.

4. CONCLUSIONS

The optimum conditions for extracting CrspEos by steam distillation were as follows: the ratio of liquid-to-solid of 8.94:1, soaking time of 199.45 min, and extraction time of 138.71 min, which resulted in the extraction yield of 47.37 μL g^{-1}. A total of 26 components were detected by GC−MS, and the Eos were composed mostly of terpenoid and aldehyde groups, including D-limonene (56.66%), myrcene (6.62%), γ-terpinene (5.69%), linalool (3.13%), *m*-cymene (3.04%), and β-citronellol (2.76%). CrspEos displayed specific adherence effect without affecting the thickness and transmittance of PS but with stronger tenacity than the raw material. CrspEos can be used as an environmentally friendly specific adhesive for PS.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00895.

GC analysis of components of CrspEos (Figure S1) (PDF)

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Notes

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