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RAPID COMMUNICATION

Synthesis of rosin allyl ester and its UV-curing characteristics

Rosin has been recognized as a potential important renewable resource in the forest chemical industry. It is a complex mixture of high-molecular-weight organic acids and related materials. The acidic constituents that make up rosin are called resin acids, which include abietic acid, neoabietic acid and palustric acid. They can be used to synthesize many types of fine chemicals,[1–3] and are widely used as raw materials to produce functional polymers.[4–8] Woo-Sik Kim[5] provided a method to synthesize poly (vinylbenzyl abietate) using poly(vinylbenzyl chloride) and sodium abietate as materials. Tae Hoon Kim[6] reported the synthesis of polymethacrylate by the reaction of poly (glycidyl methacrylate) with abietic acid. In these two methodologies, the resin derivatives were not used as monomers in the polymerization. That is, these polymers were based on the polymerization of other kinds of monomers besides resin derivatives. The final product did not provide a suitable resin structure; the conversion of the reaction was relatively low.[5–6] Moreover, a large amount of solvent was used to purify the product after reaction. Recently, vinyl compounds have become well known as photosensitive monomers. Therefore, Woo-Sik Kim[7] and Byoung-Woo Park[8] developed methods to polymerize abietate derivatives by introducing a vinylbenzyl group into the molecular structure. However, it is difficult to remove the unreacted vinylbenzyl chloride by vacuum distillation because of its high boiling point (192 °C), which would bring thermal instability to vinylbenzyl abietate.

In this study, we tried to introduce a vinyl group into the structure of rosin monomer to synthesize rosin allyl ester. The ultraviolet (UV)-curing reaction of the rosin allyl ester was investigated, and the cured product was characterized by thermogravimetry (TG), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

EXPERIMENTAL PROCEDURE
General
Materials were obtained from commercial sources and used without further purification. Infrared ray (IR) spectra (max in cm^{-1}) were obtained using a MAGNA-550 (Nicolet, Waltham, MA, USA) spectrophotometer. Gas chromatography-mass spectrometry (GC-2010, Shimadzu, Kyoto, Japan) was conducted to analyze the composition of resin acids and rosin allyl ester. Separation was performed in an HP-5 column, 30 m×0.25 mm×0.25 µm, under the following working conditions: 100 °C, 5 °C min^{-1} to 200 °C, 2 °C min to 250 °C, hold for 25 min. Acid values were determined according to the China National Standards: Test methods for rosin (GB/T 8146–2003); polymerization instrument: Intelli-ray 600 (Shenzhen Wisbay M&E Co., Ltd., Shenzhen, China) shuttered UV Floodlight (the Intelli-ray 600 utilizes a metal halide-type arc lamp and the radiation flux is 315–400 nm); wave band: 315–400 nm; intensity 100%; and timer 300 s. GPC was performed at room temperature on a Waters 515 (Waters, Milford, MA, USA) apparatus equipped with a Waters 2414 refractive-index detector. Styr-agel HR1 and HR2 (300×7.8 mm) columns from Waters were used. High-purity liquid-chromatography-grade tetrahydrofuran was used as the eluent at a flow rate of 1 ml min^{-1}. The columns were calibrated by using polystyrene standards with molecular weights in the range between 580 and 1.96×10^4 g mol^{-1} (with NMD for 1.1).

Purification of rosin acids
Twenty grams of rosin was dissolved in 15 ml acetone by stirring at 60 °C for 10 min. Then, the mixture was cooled to room temperature to obtain a solid product. The solid obtained was filtered and recrystallized twice in acetone. After purification, the total yield of the product was approximately 35% with an acid value of 182.5 mg KOH per g (185.8 mg KOH per g by theory).

Synthesis of rosin allyl ester
To obtain a solid product, 7.4 g NaOH (dissolved in 150 ml ethanol) was added dropwise to 50 g rosin acids (dissolved in 150 ml ethanol). The mixture was stirred at room temperature for 1 h and then filtered to obtain sodium rosinate. The product was dried at room temperature to produce a yield of 92.2% (49.5 g).

Rosin allyl ester was synthesized by the esterification of sodium rosinate with allyl chloride as shown in Figure 1 (abietate as representative). A mixture of sodium rosinate (10.0 g, 0.0309 mol) and allyl chloride (6.2 ml, 0.076 mol), including a trace of p-benzoquinone as a polymerization inhibitor and hexadecyltrimethylammonium bromide as phase-transfer catalyst (PTC) (0.3 g, 3% mass fraction of sodium rosinate), was heated at 40–65 °C for 6–8 h. Thereafter, unreacted allyl chloride was recovered by distillation. The mixture was cooled and filtered to produce 10.0 g of the product with a yield of 94.7%.

Polymerization
Tinplate panels (Shanghai Xiandai Environment Engineering Technique Co., Ltd., Shanghai, China) (120×50×2.8 mm) were used as substrates for film preparation. The substrates were cleaned with distilled water and acetone and then dried. The formulations were made by taking the synthesized rosin allyl ester and mixing it with 5% photoinitiator Darocure 1173 (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan). The films on the tinplate panel were irradiated under UV light to be cured; then they were stored in a dust-free cabinet for testing purposes. The UV-curing conditions were as follows: wave band 315–400 nm, intensity 100% and time 300 s[9].

RESULTS AND DISCUSSION

Recrystallization of rosin

Several types of solvent, such as ethanol, acetone, ether, ethyl acetate, trichloromethane, methylbenzene and N,N-dimethylformamide, were compared with respect to rosin recrystallization. Acetone was determined to be the most suitable solvent. The total rosin acids yield was ∼35% in rosin recrystallization. To identify the components of the rosin acids, gas chromatography–mass spectra (GC–MS) analysis was performed. The main components identified by GC–MS are illustrated in Table 1. The results show that the total rosin acids content is 98.3%.

Synthesis of rosin allyl ester

In this study, allyl chloride was chosen for reaction because of its low boiling point, which makes it easy to remove after reaction under vacuum at low temperature to avoid polymerization of the product. It can be seen that the reaction was greatly enhanced by a PTC (0.3 g, 3% mass fraction of sodium rosinate). Different types of PTCs were compared, and the most suitable catalyst was determined to be hexadecyltrimethylammonium bromide, with a product yield of 90.2%. Detailed information regarding the PTC tests is shown in Table 2.

The factors that influence the yield of the reaction, such as the amount of catalyst used, reaction time, reaction temperature and molar ratio, were investigated. The optimum reaction conditions obtained were as follows: reaction temperature 45 °C, n (sodium rosin): n (allyl chloride)=1:2.5, amount of the catalyst (hexadecyltrimethylammonium bromide) 0.3 g (3% mass fraction of sodium rosinate) and reaction time 7 h. The main components identified by GC–MS are illustrated in Table 3.

Table 3 shows that the esterification of sodium rosinate and allyl chloride was performed efficiently under a PTC to produce a total rosin allyl ester yield of 94.7% at a purity of 98.9%.

The IR spectra of rosin acids and rosin allyl ester are shown in Figure 2. The spectra clearly show that the structure of rosin allyl ester was different from that of the rosin acids. The greatest difference between the rosin acids and rosin allyl ester is the stretching of the carbonyl acid group (3000–3500 cm^{-1}). The C=C-H stretching vibrations between 3000 and 3100 cm^{-1} indicate that the allyl group was successfully introduced into the product. The C–H stretching vibrations between 2800 and 3000 cm^{-1}, and C–H deformation vibrations between 1350 and 1475 cm^{-1} indicate the presence of
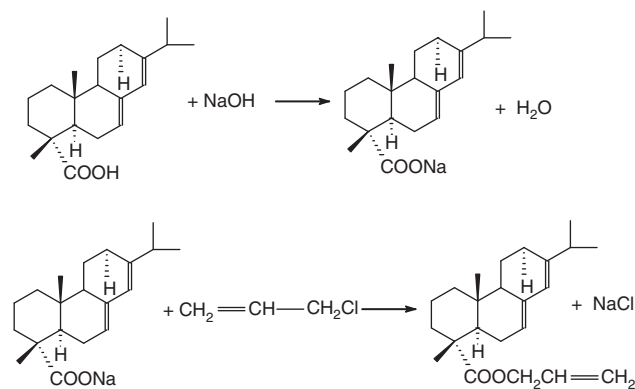

Figure 1 Synthesis of rosin allyl ester (abietate as representative).

Table 1 Results of recrystallization of rosin using acetone as solvent

Serial number	Constituents	Contents (%) in rosin	Contents after recrystallization (%)		
			First run	Second run	Third run
1	Pimaric acid	3.1	2.7	3.2	2.9
2	Pinus elliottii acid	3.0	1.4	0.7	0.3
3	Sandaracopimaric acid	1.9	1.6	2.1	1.9
4	Isopimaric acid	13.0	14.0	13.2	15.2
5	Palustric acid and levopimaric acid	22.8	23.5	23.3	21.7
6	Dehydroabietic acid	3.6	4.1	4.2	5.2
7	Abietic acid	26.0	32.1	36.9	41.7
8	Neoabietic acid	19.8	16.2	14.1	9.4
	Total (%)	93.2	95.6	97.7	98.3

Table 2 Effect of different kinds of catalyst on product yield

Catalyst	Yield of product (%)
Blank	69.7
Hexadecyltrimethylammonium bromide	90.2
Tetrabutylammonium chloride	87.0
Tetrabutylammonium bromide	79.0
Tetraethylammonium bromide	83.8
Tetracesium 4,4'-carbonylbisphthalate	83.3

Table 3 Main components in rosin allyl ester

Constituents	Retention time (min)	Contents (%)
Allyl pimarate	43.9	1.4
Allyl pinus elliottiate	44.1	1.0
Allyl sandaracopimarate	44.6	0.9
Allyl isopimarate	45.8	11.9
Allyl palustriate	46.3	16.2
Allylevopimarate	46.6	1.2
Allyl dehydroabietate	47.3	5.0
Allyl abietate	49.1	56.8
Allyl neoabietate	51.8	4.5
Total		98.9

methyl and methylene in the rosin structure. The presence of an olefinic group is confirmed by the band at 1650 cm^{-1}, arising from the C=C stretching vibration mode. Moreover, C=O stretching vibrations with absorbance at 1720 cm^{-1} and C-O stretching vibrations with absorbance between 1100 and 1300 cm^{-1} indicate that there is an ester group in the product. The IR analysis is in good agreement with the results of GC–MS studies.[10]

Polymerization

The photopolymerization of rosin allyl ester was examined using tetrahydrofuran as a diluent (50%) and Darocure 1173 (5%) as a photoinitiator upon irradiation with UV light. The obtained film (that is the UV-cured resin) was characterized by TG, DSC and GPC, the results of which are shown in Figures 3–5.

Figures 3 and 4 provide the thermal analysis (TG and DSC) results for the cured resin. We tried to use TG analysis to evaluate the thermal stability, and it was found that the initial decomposition temperature of the product is 264 °C (Figure 3). Therefore, it can be assumed that the product derived from rosin allyl ester has good thermal stability. The DSC analysis results shown in Figure 4 for the cured resin from rosin allyl ester indicate that the glass transition temperature is 24 °C. This result suggests that the obtained UV-cured coating may possess superior properties in terms of flexibility, impact strength and adhesion to form a low transition temperature homopolymer monomer, typically called a soft monomer.

Figure 5 provides a GPC chart of the UV-cured resin produced from rosin allyl ester. The values of the GPC analysis of the cured product are given in Table 4. It can be seen that the cured product, photoinitiated by Darocure 1173, produced number-average molecular weights between 630 and 12 536 kDa with polymerization degrees between 2 and 37. The results show that the cured resin provided a wide molecular-weight distribution. Moreover, a small fraction of unreacted monomers (15.6%) was observed in the product. Further studies on this reaction, such as improving the conversion of monomers and using high-reactive monomers in the copolymerization reaction, are needed and are currently under investigation in our research group. From these photochemical data, we concluded that the product photopolymerized from rosin allyl ester might be expected to be a novel and thermally stable material.

A plausible mechanism for the polymerization is shown in Figure 6. The polymerization
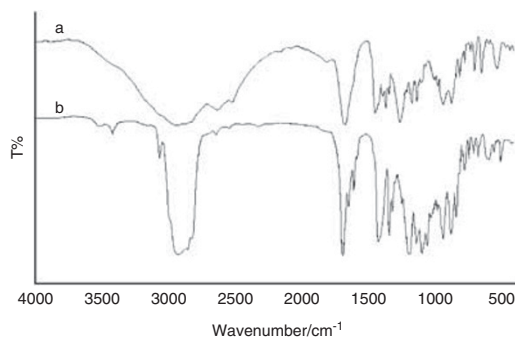

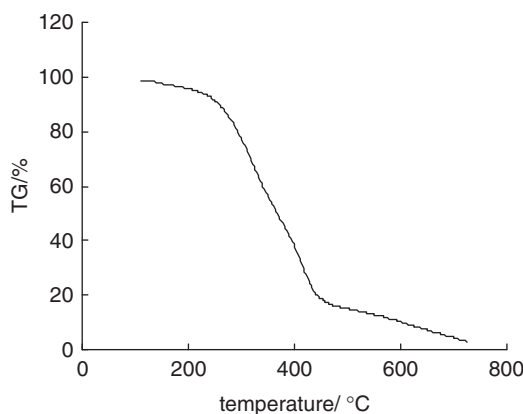Figure 2 Infrared analysis of rosin acids (a) and rosin allyl ester (b).

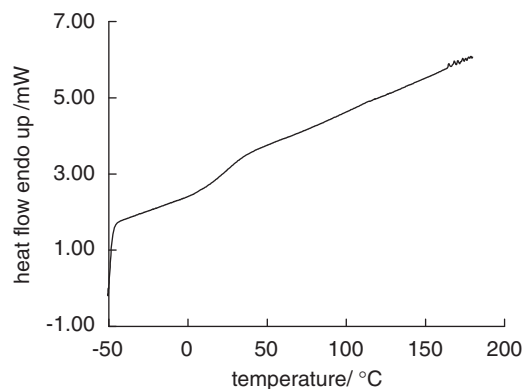Figure 3 Thermogravimetry curve of the cured resin.

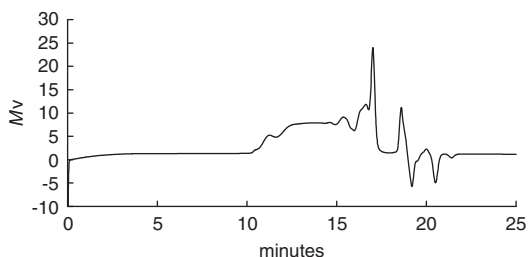Figure 4 Differential scanning calorimetry curve of the cured resin.


Figure 5 Gel permeation chromatography chart of the cured resin obtained from rosin allyl ester.

Table 4 Cured product using Darocure 1173 as photoinitiator

Serial number	Retention time (min)	M_n	M_w	M_p	M_z	M_{z+1}	M_w/M_n	Polymerization degree	Area (%)
1	11.3	12 536	14 008	11 693	16 067	18 710	1.1	37	37.2
2	13.6	2296	3027	1776	3999	4959	1.3	7	8.4
3	14.6	981	990	1005	998	1007	1.0	3	15.8
4	15.4	630	646	658	663	679	1.0	2	15.8
5	16.6	357	363	320	370	376	1.0	1	15.6

Abbreviations: M_n, Number-average molecular weight; M_w, weight-average molecular weight; M_z, z-average molecular weight; M_p, molecular weight; M_w/M_n, polydispersity index (molecular weight distribution).
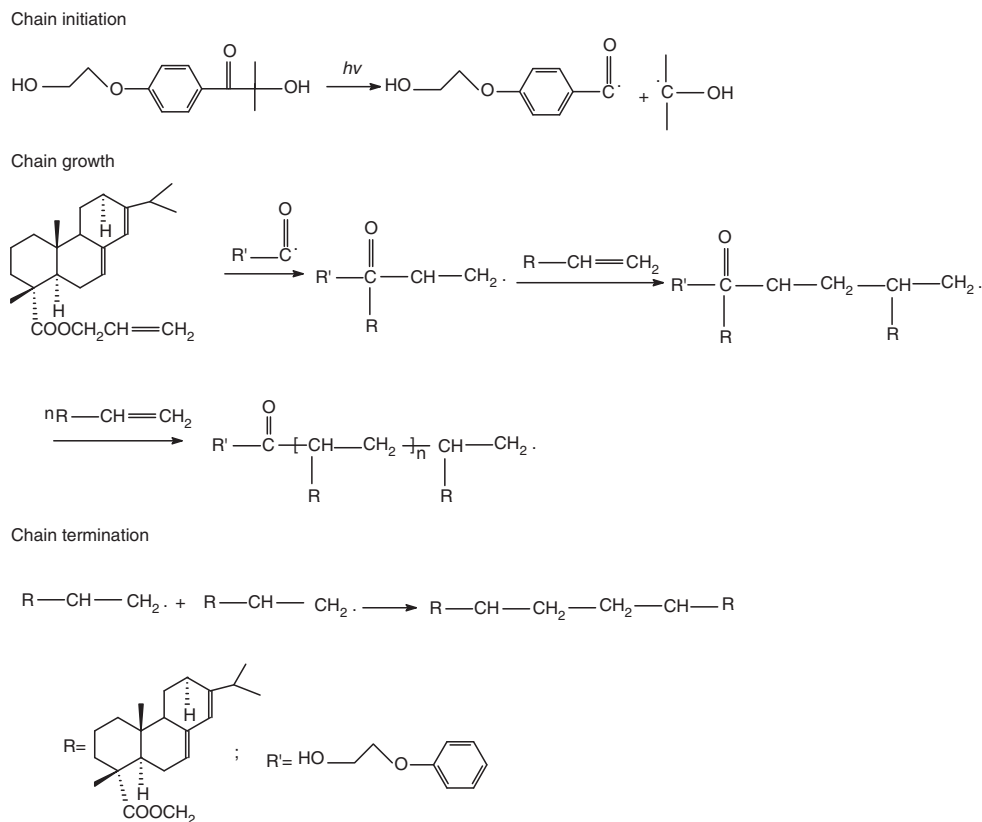
Figure 6 Reaction mechanism of polymerization.

reactions using novel monomer (rosin allyl ester) can be described by the following steps:

(1) Chain initiation: Photopolymerization initiators absorb UV, and these photopolymerization initiators that have absorbed UV light are excited and cleaved into two radicals.
(2) Chain growth: Activated photopolymerization initiators react with rosin allyl ester and a chain reaction proceeds. Then, the molecular weight increases, and the resin are cured.
(3) Chain termination: During chain growth polymerization, two growing chains can collide head to head, terminating the growth of both chains.

CONCLUSIONS

1. Purified rosin acid was obtained by repeated recrystallization using acetone as a solvent for three times. The total rosin acids yield was approximately 35%, with an acid value of 182.5 mg KOH g^{-1}.
2. Rosin allyl ester was synthesized using sodium rosinate and allyl chloride as raw materials. Under the optimum reaction conditions, the ester yield was as high as 94.7%. The structure of the ester was identified by GC–MS and Fourier transform Infrared.
3. The UV-cured resin obtained from the photopolymerization of rosin allyl ester was characterized by TG, DSC and GPC.

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