

Synthesis of a Tung Oil-Rosin Adduct via the Diels–Alder Reaction: Its Reaction Mechanism and Properties in an Ultraviolet-Curable Adhesive

Jianbing Wu,^{1,2} Tong Zhang,^{1,2} Guozhang Ma,² Ping Li,² Lixia Ling,³ Baojun Wang¹

¹Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China

²Shanxi Research Institute of Applied Chemistry, Taiyuan, Shanxi 030027, China

³Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China

Correspondence to: B. Wang (E-mail: wangbaojun@tyut.edu.cn)

ABSTRACT: A Diels–Alder adduct of rosin with tung oil was effectively prepared for use as a filler and adhesion promoter in UV-curable adhesives. The characteristics of the adduct were analyzed by Fourier transform infrared (FTIR) spectroscopy and ultraviolet–visible (UV–vis) absorption spectra. The reaction mechanism was studied with gel permeation chromatography, thermogravimetric analysis, ¹H-NMR, and the density functional theoretical method. The FTIR and ¹H-NMR results showed that the Diels–Alder addition occurred between the rosin and tung oil. The still-existing characteristic peaks of the conjugated diene in the adduct, as shown in the FTIR and UV–vis absorption spectra, indicated that the most favorable reaction between the rosin and tung oil was when the rosin was used as the conjugated diene and the tung oil was used as the dienophile. The molecular weights of the adduct with different molar ratios showed that the most possible addition molar ratio between the rosin and tung oil was 3:1. The favorable addition mechanism was further proved by a comparison of the relative energies of different isomers of the adduct with theoretical calculation, and the most stable structure of adduct showed that the addition position of tung oil was the terminal C=C double bond. The properties analysis indicated that the adduct could improve the adhesion of UV-curable adhesives and reduce the curing shrinkage rate. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 4201–4208, 2013

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INTRODUCTION

In recent years, more and more natural, renewable materials have attracted a lot of attention as raw materials for the preparation of polymers and resins to replace traditional petrochemical-based polymers.^{1,2} Polymers prepared from natural materials have been comprehensively used in organic coatings,³ ink,⁴ and other applications.

Rosin is an abundantly natural product that is obtained directly from pine trees. Rosin acids are composed of abietic-type resin acids with conjugated double bonds and a single carboxylic group; there are thought to be four abietane-type rosin acid isomers in conversion according to the literature, including abietic acid, plustric acid, levopimaric acid (LEA), and neoabietic acid.⁵ Rosin, being one of the important renewable resources, has been extensively used as a raw material in the preparation of some new polymers in adhesives, varnishes, and printing ink.⁶ In particular, rosin is an effective adhesion promoter and viscosity controller. Therefore, it is expected that adhesive, stable,

transparent, and thermally stable polymer films will be obtained when a rosin moiety is incorporated into the polymer structure.⁷ However, rosin is a multiple rigid-cycle structure; it is often used in a chemically modified form by means of a Diels–Alder cycloaddition reaction to prepare difunctional or multi-functional monomers of polyesters with maleic anhydride,⁸ acrylic acid and acrylates,⁹ Fullerene C₆₀,¹⁰ amine, and so on. The abietic acid will isomerize as LEA at high temperatures and can be used as a conjugated diene in a Diels–Alder reaction.¹¹

Tung oil is one of the main drying oils and has been found to have numerous applications in the paint industry. Its main component is a glyceride of elaeosteric acid (*cis*-9, *trans*-11, *trans*-13-octadecatrienoic acid) with a conjugated triene structure; it is easily available from the seeds of the tung tree. Unlike most seed oils, tung oil is conjugated. Consequently, tung oil can be used to accelerate the drying time, enhance the water resistance and hardness by copolymerization and Diels–Alder addition, and so on. Tung oil has been polymerized by both free-radical, cationic and thermal conditions and can also be

copolymerized with styrene and divinylbenzene.^{12,13} In recent years, copolymers synthesized from tung oil and diacrylate by Diels–Alder addition have been reported, and the copolymers have been readily prepared and have exhibited good solvent resistance, high hardness, good gloss, and fast curing speeds in the UV curing process.^{14,15}

However, both the rosin and tung oil also present a high degree of unsaturation; either of them can be used as a conjugated diene or dienophile in the Diels–Alder addition reaction. More and more polymers based on rosin^{8,16} or tung oil^{17,18} have been prepared via Diels–Alder addition. However, there have been few reports about the reaction mechanism between two conjugated dienes,¹⁹ especially rosin and tung oil.

The aim of this study was to examine the Diels–Alder addition mechanism between the tung oil and rosin by Fourier transform infrared (FTIR) spectroscopy, ultraviolet–visible (UV–vis), thermogravimetric analysis (TGA), ¹H-NMR, and the density functional theoretical (DFT) method. In addition, the effect of the product on the adhesion strength and curing shrinkage rate of UV-curable adhesives was investigated.

EXPERIMENTAL

Materials

Rosin with an acid number of 162 mg of KOH/g (Guangxi Qipo Rosin Co., China) and tung oil (Hubei Yuxing Chemical Co., Inc., China) were used to synthesize an adduct. Hydroquinone (Sigma Aldrich) was used as an inhibitor. Epoxy acrylate with double functionality from UCB Chemicals was used as an oligomer. Isobornyl acrylate and 1,6-hexanediol diacrylate from UCB Chemicals were used as monomers, and 1-hydroxycyclohexylphenyl ketone (Irgacure184) from Ciba-Geigy was used as a free-radical photoinitiator. All of the chemicals were used as received without further purification. The other chemicals were analytical reagents and were purchased locally.

Preparation of the Diels–Alder Adduct from Rosin and Tung Oil

The weighed rosin was melted at 170°C for 0.5 h in a 500-mL, four-necked flask equipped with a mechanical stirrer, a nitrogen purging system, a thermometer, and a refluxing device; then, a certain amount of tung oil was added slowly to the flask, and the mixture was stirred for a certain time vigorously at 170°C under a nitrogen atmosphere. A concentration of 0.5 wt % of hydroquinone was added to the system to prevent polymerization during the reaction process. The low fraction was removed under reduced pressure for 15 min to yield a yellowish solid. Then, every 100 g of solid mass was dissolved in 100 mL of CHCl₃, and the polymers were precipitated by the addition of an eightfold excess of CH₃OH into the solution. The polymer was purified by two reprecipitations from CHCl₃ into CH₃OH. The polymers were dried *in vacuo* at 35° for 96 h and then weighed to determine the conversions.¹⁷

Preparation of the UV-Curable Adhesive with the Adduct

The neat UV-curable adhesive used in this study was a mixture of 30 wt % epoxy acrylate, 40 wt % isobornyl acrylate, 25 wt % 1,6-hexanediol diacrylate, and 5 wt % Irgacure 184. Concentrations of 2, 4, 6, and 8 wt % of adduct were directly added to

the previous mixture and blended under stirring at room temperature. The modified UV-curable adhesives were obtained.

Instrument and Characterization

FTIR spectra were recorded on a Nicolet 360 FTIR spectrometer with KBr pellets. UV–vis absorption spectra were recorded with a UV–vis absorption spectrophotometer (Shimadzu, UV-3100PC). The molecular weights of the products and the square ratio of different components were determined by gel permeation chromatography (GPC) equipped with a Waters 1515 isocratic high performance liquid chromatography (HPLC) pump and a 2410 refractive index detector. THF was used as the solvent, and numerical values for the molecular weights were generated by comparison to a polystyrene calibration curve. ¹H-NMR analysis was performed with a Bruker Avance DRX 300 instrument at 300 MHz. The spectra were referenced to internal tetramethylsilane. The samples were dissolved in CHCl₃. The viscosity was tested by an NDJ-79 rotation viscometer (Shanghai Scientific Instrument Co., China). An amount of 2 g of the product was dissolved in 2 mL of refined linseed oil at 150°C according to the weight proportion of 1:1 to prepare the linseed oil solution, and the viscosity of the solution was determined at 25°C. TGA was carried out on an HCT-1 thermogravimetric analyzer (Henven Scientific Instrument Co., China) at a heating rate of 20°C/min from 20 to 800°C at a nitrogen flow speed of 50 mL/min.

To measure the volumetric shrinkage of the UV-curable adhesives, the adhesives samples were glued onto glass substrates and cured by spot curing equipment with approximately 80 mW/cm² for 300 s. The volumetric shrinkage of the sample was determined by the measurement of the density change of each resin sample before and after UV curing according to the following equation:²⁰

$$\text{Shrinkage (\%)} = \frac{1/d_{\text{after}} - 1/d_{\text{before}}}{1/d_{\text{before}}} \times 100\%$$

where d_{before} is the density of the sample before curing and d_{after} is the density of the resin after curing. The densities of the cured samples were determined by the displacement method with a Mettler AX105DR density determination kit.

For the adhesion test, the adhesive was applied onto the 7 × 7 mm² glass surface and glued onto another glass plate with adhesion area of 7 × 3 mm². The measurement was performed on an electronic tensile meter (Shenzhen Sans Testing Machine Co., Ltd., China) at room temperature with a crosshead speed of 2 mm/min.

Theoretical Calculation

The DFT method was adopted and calculations were performed with the Dmol³ program²¹ mounted on the Materials Studio 5.5 package. The reactant, intermediates, and products were optimized at the level of the generalized gradient approximation with the Perdew–Wang 1991 (PW91) functional²² and doubled numerical basis set plus polarization basis sets (DNP) basis set. Spin unrestricted was chosen, and the total self consistent field (SCF) tolerance criteria, integration accuracy criteria, and orbital cutoff quality criteria were set at medium. Multipolar expansion was set at octupole. The tolerances of energy, force,

and displacement convergence were 2×10^{-5} hartree, 4×10^{-3} hartree/Å, and 5×10^{-3} Å, respectively. All of the calculations were performed on a Dell Pentium D PC server system.

To evaluate the reliability of the selected calculation method and parameters, the total energies of the four abietic-type resin acids in rosin were calculated. The results show that abietic acid was the most stable structure and LEA was the most active; this was in agreement with the theoretical and experimental results.^{11,23,24} The tung oil acid was chosen as a substituted model of tung oil because of the calculation time and the tung oil structure.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Tung Oil Modified Rosin

The Diels–Alder addition between the rosin and tung oil was complex because at least four rosin isomers and two tung oil isomers existed. Therefore, the main goal of this study was to provide the most favorable reaction mechanism, including a qualitative analysis of which was a dienophile or conjugated diene and quantitative evidence of the ratio between the rosin and tung oil during the Diels–Alder reaction. Different molar ratios between the rosin and tung oil were chosen to determine two different reaction mechanisms. When rosin is used as a conjugated diene, tung oil provides at most nine molar-equivalent C=C double bonds used as a dienophile, so the molar ratios between the tung oil and rosin chosen were 1:3, 1:6, and 1:9. On the contrary, the tung oil provided at most three conjugated dienes to react with the rosin used as a dienophile, and the corresponding molar ratio between tung oil and rosin was 1:3.

Temperature is an important parameter in Diels–Alder addition. LEA probably isomerized directly to other resin acids irreversibly at temperatures lower than 155°C or higher than 200°C according to the literature.⁶ The reaction temperature of castor oil or tung oil with other dienophiles is 150–170°C.²⁵ Therefore, different molar ratios of tung oil to rosin were investigated at 170°C for 4 h according to Diels–Alder addition between rosin and other materials.⁶

The absorbing peak differences between the primary material and the product are shown in Figure 1. In the FTIR spectrum of the rosin (curve a), the broad absorption bands in the range 2300–3500 cm^{-1} were specific to the OH stretching absorption of carboxylic acid and aliphatic carbon–hydrogen absorption due to the hydrogen bonding of rosin acid. Meanwhile, an absorption peak at 2651 cm^{-1} appeared for hydrogen bonding, and the peak for the carbonyl group was located at a lower frequency at 1694 cm^{-1} . The FTIR spectrum of tung oil (curve b) showed a sharp shoulder peak at 3010 cm^{-1} ; this corresponded to the trans–trans conjugated unsaturations. The existence of a strong peak at 990 cm^{-1} was also assigned to the presence of the trans–trans conjugation in the elaeostearic chains. The small peaks at 964 and 735 cm^{-1} were the result of the presence of cis unsaturations.²⁶ The peak at 1745 cm^{-1} was assigned to the ester carboxylic group in triglyceride molecules. The occurrence of a Diels–Alder reaction between the rosin and tung oil was illustrated by the appearance of a strong absorption band at 3443 cm^{-1} , which corresponded

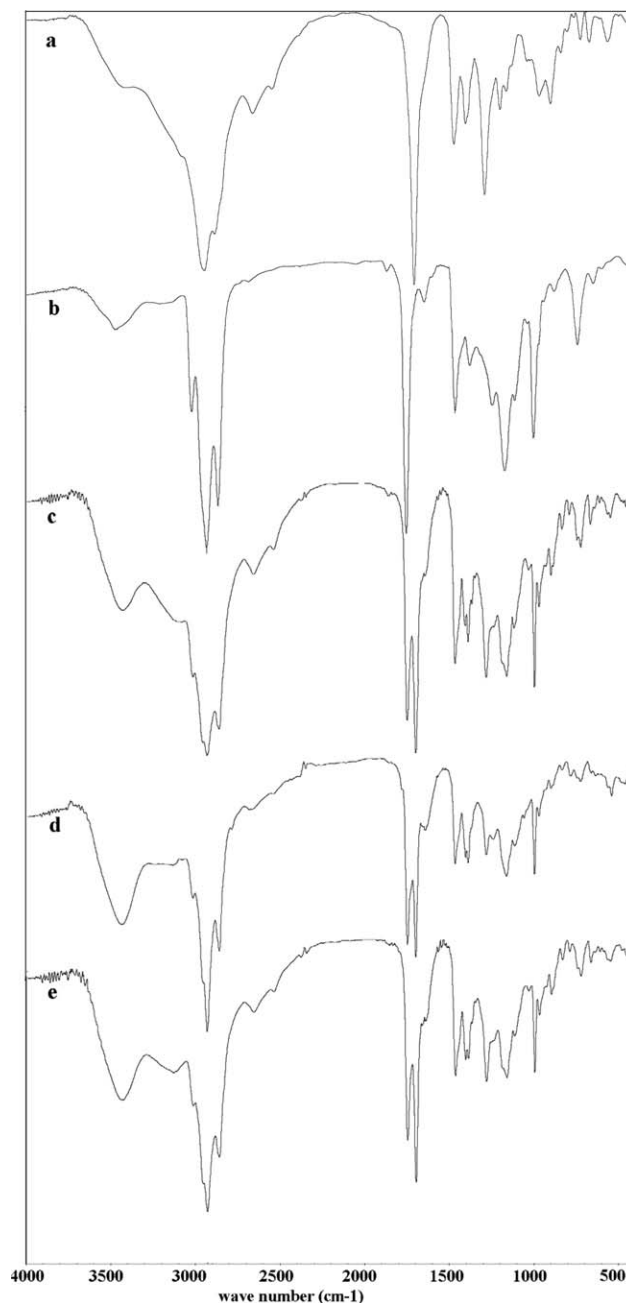


Figure 1. FTIR spectra of (a) rosin, (b) tung oil, and adducts with tung oil to rosin molar ratios of (c) 1:3, (d) 1:6, and (e) 1:9.

to the COOH group of the rosin. The significant intensity decrease of the peaks at 3010, 990, and 763 cm^{-1} corresponded to the conjugated diene of tung oil [Figure 1(c–e)]. However, the characteristic signals of the conjugated diene, corresponding to tung oil, still existed in the FTIR spectrum of the adduct structure with molar ratios of tung oil to rosin from 1:3 to 1:9. When the tung oil was used as a conjugated diene in the Diels–Alder reaction, because of the excessive rosin, there were no characteristic peaks of the conjugated diene structure corresponding to tung oil in the final product.

UV–vis absorption spectra were used to determine the isomerization of rosin and the change in the maximum absorption

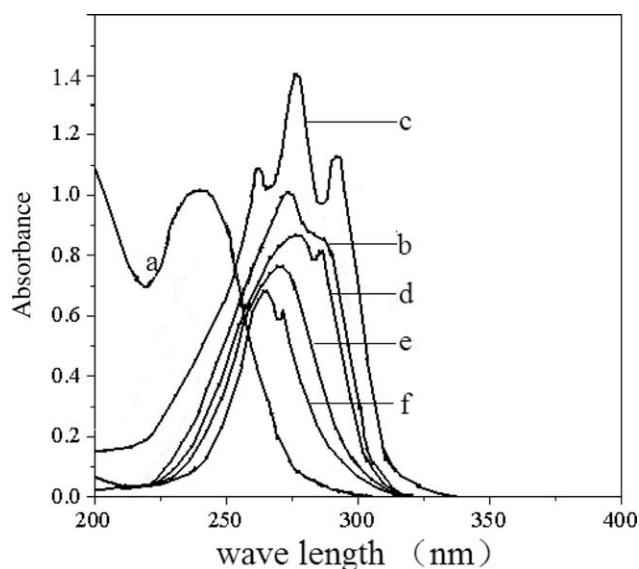


Figure 2. UV absorption spectra of the (a) primary rosin, (b) rosin after 4 h at 170°C, (c) tung oil, and adducts with tung oil to rosin molar ratios of (d) 1:3, (e) 1:6, and (f) 1:9.

peak with different molar ratios of tung oil to rosin. Figure 2 shows the UV absorption spectra of the primary material and the product. The maximum absorption peak of rosin appeared at 241 nm, whereas the maximum absorption peak appeared at 270 nm with a large redshift after 4 h at 170°C; this indicated that the hydroabietic acid structure of rosin was converted to LEA.²⁷ Strong absorption bands at 261, 271, and 282 nm were observed in the UV-vis absorption spectra; these corresponded to its higher unsaturation and conjugated triene. The maximum

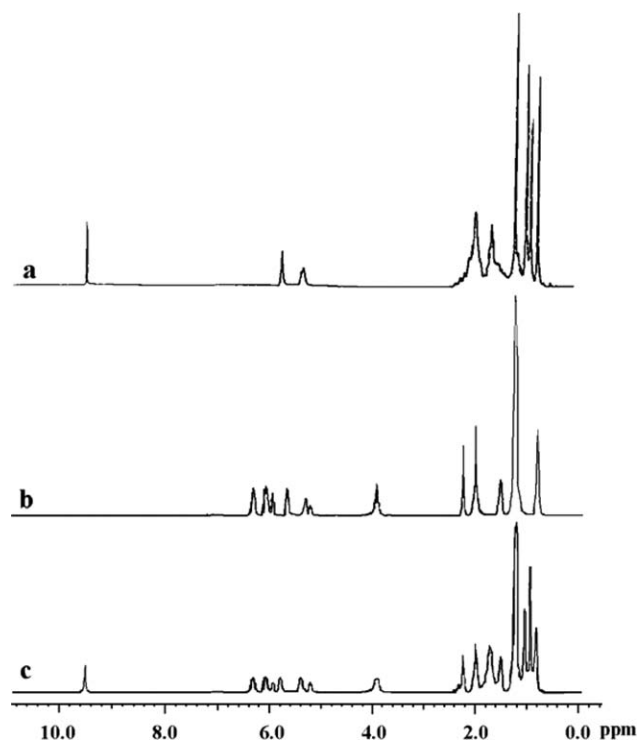


Figure 3. ¹H-NMR of the (a) tung oil, (b) rosin, and (c) adduct with a tung oil to rosin molar ratio of 1:3 at 170°C for 4 h.

absorption band of the adduct decreased and was distorted with increasing amount of rosin; this was ascribed to the decrease in the unsaturation degree. We concluded that there were still conjugated diene structures in the adduct with different ratios, and the characteristics absorption bands could be assigned to the conjugated diene of tung oil.²⁸ When the middle double bonds of tung oil reacted with rosin, there was not a conjugated diene structure. The double bonds close to the carbonyl group of tung oil may not have reacted with rosin because of steric hindrance, so we inferred that the most possible addition position of tung oil was the terminal double bond, and the chance for the three chains of tung oil was the same. Of course, there may have been side reactions between the tung oil and rosin, including self-polymerization and different addition modes. We only considered the main reaction and the most possible reaction mechanism in this study.

Figure 3 shows the ¹H-NMR of the tung oil, rosin, and adduct with a tung oil to rosin molar ratio of 1:3 at 170 for 4 h. The assignments were made by comparisons to literature spectra^{2,6} and by computer simulation. In the spectra of adduct, the reaction was reflected by the appearance of the bands in the chemical shift of 9.3 and 4.0 ppm; these could be ascribed to the carboxylic acid of rosin and the methylene of the tung oil. The signals in the complex series of peaks in the range from 0.85 to 2.5 ppm were assigned to the methyl, methylene, and methine groups from the rosin and tung oil. These partly overlapped in the field 2.3–2.5 ppm with the methine groups of the rosin adjacent to the tung oil linkage. The signals in the chemical shift range of 5.3–5.5 ppm were due to the vinyl protons in the rosin and tung oil. In the spectrum of the tung oil, the resonance signal range from 6.4 to 6.6 ppm was characteristic of conjugated triene group signals. In the spectrum of the adduct, as expected, this disappeared, and the signal characteristics of ethylene were present at 6.0 and 5.8 ppm; this indicated that the conjugated triene structure of the tung oil was damaged, but the conjugated diene still existed during the Diels–Alder addition.

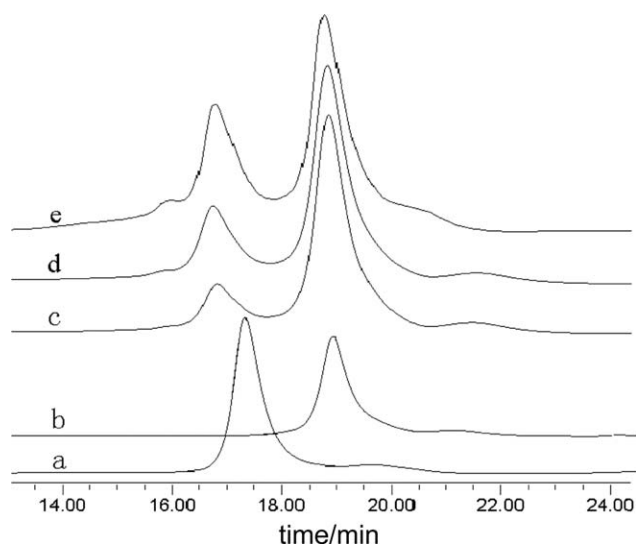


Figure 4. GPC curves of the (a) tung oil, (b) rosin, and adducts with molar ratios of tung oil to rosin of (c) 1:3, (d) 1:6, and (e) 1:9.

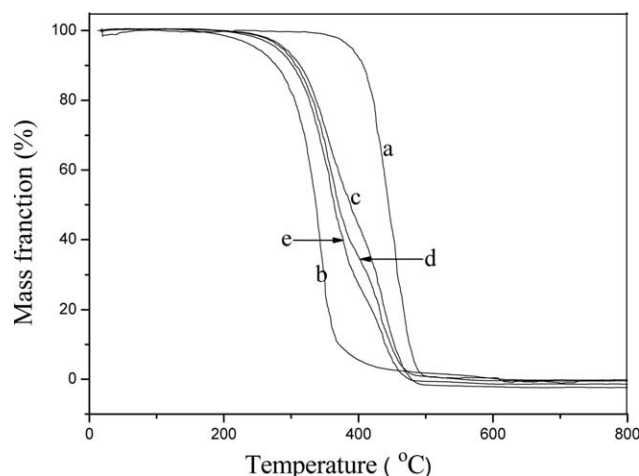


Figure 5. TG curves of the (a) tung oil, (b) rosin, and adducts with molar ratios of (c) 1:3, (d) 1:6 and (e) 1:9.

The GPC analysis was an effective tool to determine whether one polymer reacted with the other or not. The GPC results of the adduct with different ratios are as shown in Figure 4. The molecular weight change, as shown in Table I, affirmed that the Diels–Alder addition between the rosin and tung oil occurred. The peaks at about 17 min with a molecular weight of about 1400–1600 were attributed to the adduct because the theoretical molecular weights of both the tung oil and rosin were no greater than 1000, whereas the peaks at about 19 min with a molecular weight of about 550 belonged to the incomplete esterification of tung oil or rosin aggregation. The average molecular weight of the adduct changed little when the molar ratio of tung oil and rosin changed from 1:3 to 1:9; the weight-average molecular weight (M_w) was 1400–1700. This was close to the sum of one tung oil molecular weight ($M_{\text{tung oil}} = 782$ g/mol) and three rosin molecular weights ($M_{\text{rosin}} = 302$ g/mol). On the basis of the spectral results and the change in the average molecular weight, we inferred that the molar ratio of tung oil to rosin was 1:3 during the reaction. More rosin could not be added to the tung oil molecule because of steric hindrance. However, the weak shoulder peak at 16 min decreased from 1:3 to 1:9; this indicated that more rosin in the addition system reduced the polymerization probability of tung oil, and further addition reaction may have been very difficult. The viscosity change also proved that the greater the amount of rosin there was in the addition system, the larger the viscosity was because of large-scale unreacted rosin molecules existing in the system. The conversion decreased with increasing amount of rosin; this

Table I. Different Adducts Based on Tung Oil and Rosin with Molar Ratios of (a) 1:3, (b) 1:6, and (c) 1:9

Sample	Viscosity (mPa s at 25°C)	M_n	M_w	Area ratio	Conversion (%)
a	12,000	1268/534	1428/536	1:1.5	72.3
b	17,000	1443/556	1766/562	1:3	68.4
c	21,000	1434/576	1681/585	1:5	55.7

Table II. TG Data for the Different Adducts, Tung Oil, and Rosin

	T_5 (°C)	T_{10} (°C)	T_{50} (°C)
a (1:3)	289.5	314.0	390.0
b (1:6)	283.9	305.6	371.0
c (1:9)	276.5	301.1	364.9
Tung oil	388.5	406.2	443.5
Rosin	247.6	277.5	336.6

indicated that more rosin could not react with tung oil and still act as a monomer.

The thermal behavior of adducts was evaluated by TGA, and the results are shown in Figure 5 and Table II. We observed that the nonisothermal decomposition process consisted of a single stage for the adducts. The thermogravimetry (TG) curves showed a continuous weight loss in the temperature range of 220–470°C; this corresponded to the scission of the ester linkage and the hydrophenanthrene structure of the rosin. However, the greater the amount of rosin was, the lower decomposition temperature of the adduct was; this was ascribed to the thermal instability of the rosin at high temperatures.

The temperature of weight loss of 5% (T_5), temperature of weight loss of 10% (T_{10}), and temperature of weight loss of 50% (T_{50}) values of the adducts and materials are listed in Table II. We observed that the decomposition temperature decreased with increasing content of rosin during the addition process. This confirmed that the decomposition reaction of the adducts was very complex, with the participation of at least three compositions, including the addition product, unreacted tung oil, and rosin, and two different mechanisms²⁷ during thermal decomposition. The first thermal degradation stage, situated between 220 and 280°C, with a mass loss of about 5 wt %, was attributed to the decomposition of COOH groups bonded to hydrophenanthrene moieties. The second stage of thermal degradation, situated between 300 and 470°C, was due to the remaining COOH groups and the decomposition of maleic and hydrophenanthrene moieties. According to the previous results, we thought that the Diels–Alder addition between tung oil and rosin occurred, and the TG curves also proved the linkage between them.

Theoretical Results for the Addition Reaction Between Tung Oil and Rosin

The previous experimental results show the feasibility and possibility of Diels–Alder addition between tung oil and rosin. The

Table III. Relative Energies (E_{re} Values) of the Different Structures

Structure	E_{re} (kJ/mol)	Structure	E_{re} (kJ/mol)	Structure	E_{re} (kJ/mol)
TYS (1)	0.00	P1	0.00	P4	84.24
TYS (2)	8.73	P2	30.15	P5	63.09
TYS (3)	3.36	P3	25.81	P6	83.03
TYS (4)	4.12			P7	99.38

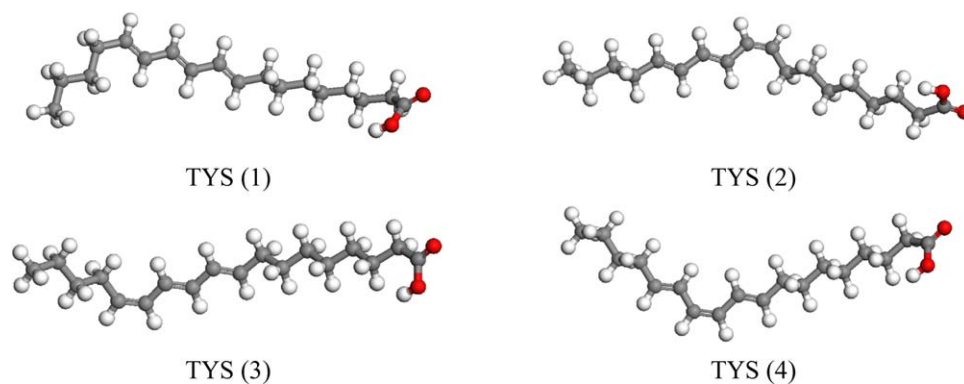


Figure 6. Possible structure of the tung oil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

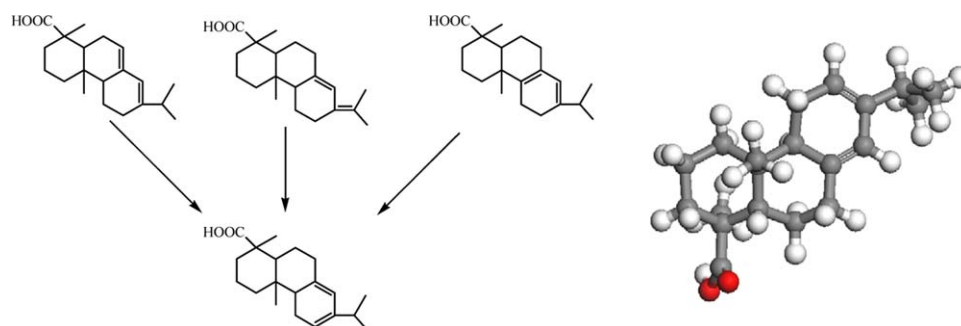


Figure 7. Structural changes between the rosin isomers and the structural model of LEA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

experimental results of the possible reaction mechanism were further investigated by the DFT method.

For tung oil, tung oil acid (TYS) instead of tung oil was chosen for this study. Four possible structures for YYS were obtained [TYS (1), YYS (2), YYS (3), and YYS (4)] and are shown in

Figure 6, and the relative energies to YYS (1) are listed in Table III. We observed that YYS (1) was the most stable, and it is the main form of tung oil.

LEA was the most active structure for rosin isomers; this was in good agreement with the experimental results and previous

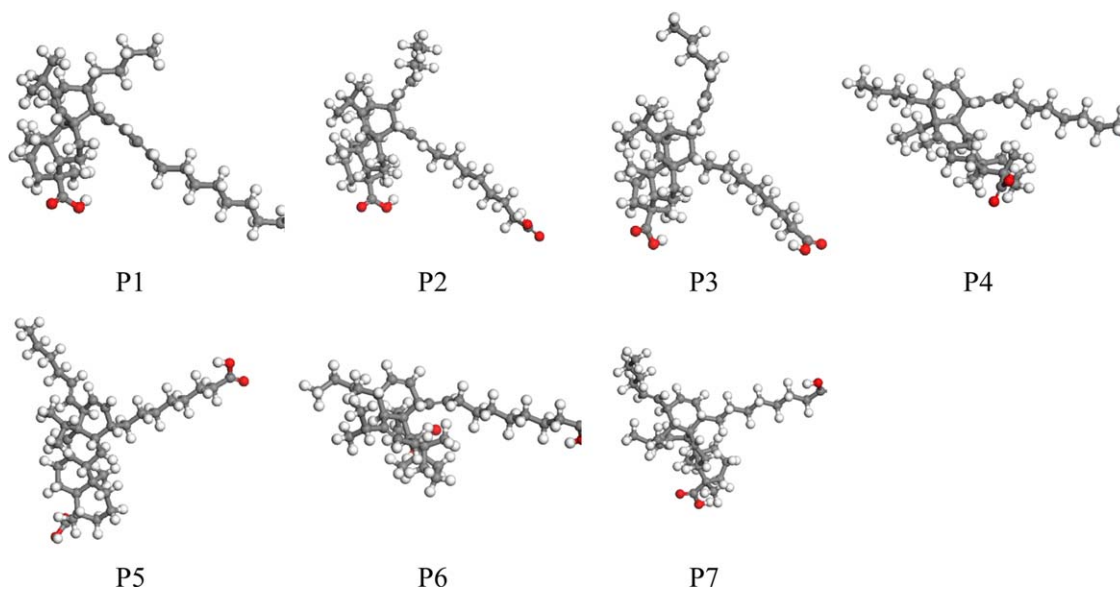


Figure 8. Structure of the possible final product. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

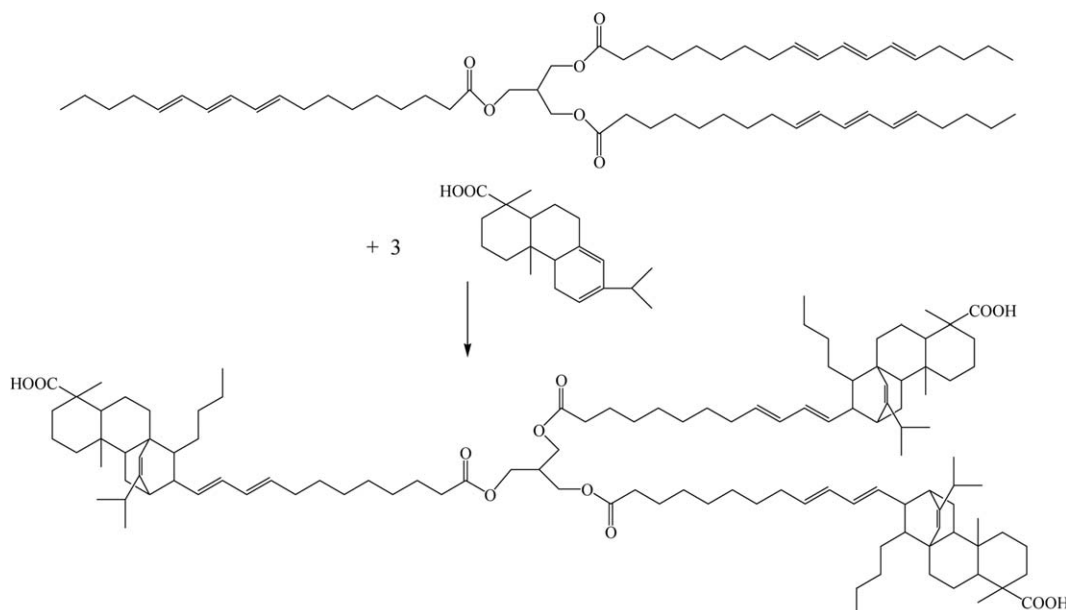


Figure 9. Idealized Diels–Alder addition scheme between the rosin and tung oil.

research. During the reaction process, all of the isomers of rosin converted to LEA to provide a conjugated diene in the Diels–Alder reaction, as shown in Figure 7.

Seven possible configurations (P1–P7) for the product by the reaction of TYS (1) and LEA were obtained and are shown in Figure 8, and their relative energies to P1 are also listed in Table III. In P1–P3 as shown in Figure 8, LEA provided a conjugated diene, and TYS acted as the dienophile structure. In P4–P7, TYS provided a conjugated diene, and LEA provided the dienophile structure. P1 was the most stable structure and was formed by the reaction of a conjugated diene in LEA and the terminal alkene bond in TYS.

According to the experimental research and theoretical calculation, the most possible addition mechanism between tung oil and rosin was that the conjugated diene structure of rosin reacted with terminal double bonds of the tung oil at a molar ratio of 3:1, and the reaction scheme is represented in Figure 9.

Properties of an Adduct in UV-Curable Adhesive

Polymerization leads to an increase in the density of a material and to volumetric shrinkage. Typical values for this increase in acrylates are 10–15%. However, the specific molecular structure has a major impact on the extent of the shrinkage.²⁹ It has been reported that the polymerization shrinkage value decreases when the molecular volume is increased,³⁰ and the amount of shrinkage could be reduced to some extent by increasing the filler content.³¹ Figure 10 shows the shrinkage and adhesion strength variation with the amount of the resulting adduct in UV-curable adhesives; in the initial stage, the shrinkage of the adhesives sharply decreased with increasing amount of adduct, but it stabilized after further increases in the adduct amount. This was ascribed to the fact that volumetric shrinkage stress could be released by the cyclic structure of rosin, and the long-chain structure increased the flexibility of the adhesive. How-

ever, the adhesion strength of the UV-curable adhesives first increased and then decreased with increasing amount of tung oil modified rosin; this was due to the fact that the carboxyl group of rosin could corrode the glass surface or form hydrogen on the glass surface. However, more adduct was used as filler and could not participate in the photopolymerization, so the adhesion decreased. We concluded that the best concentration of adduct in the UV-curable adhesives was 4 wt %.

CONCLUSIONS

The incorporation of experimental and theoretical results showed that the Diels–Alder addition between rosin and tung oil occurred at a molar ratio of 1:3, the terminal double bonds of tung oil were used as a dienophile, and LEA isomerized from rosin was used as a conjugated diene in the Diels–Alder addition. The adduct could be used as a filler and adhesion

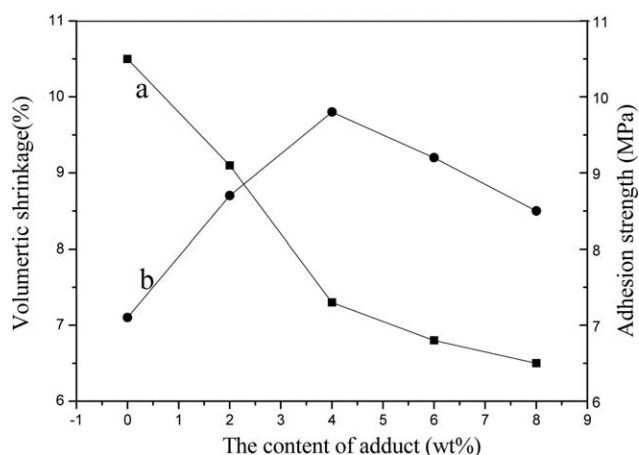


Figure 10. Effect of the adduct on the volumetric shrinkage and adhesion strength of the UV-curable adhesives.

promoter in UV-curable adhesives. The volumetric shrinkage and adhesion strength of the UV-curable adhesives were also improved because of the special structure characteristics of the adduct, although a higher amount led to a decrease in the adhesion strength of the UV-curable adhesives because the obtained adduct could not participate in the film-formation process.

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