Designing Rosin-Based Plasticizers: Effect of Differently Branched Chains on Plasticization Performance and Solvent Resistance of Flexible Poly(vinyl chloride) Films

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ABSTRACT: In the present study, we report a strategy to prepare rosin-based plasticizers with differently branched chains, which have the same benzene ring and similar alkane structure compared to phthalate plasticizers. Castor oil methyl ester, cardanol, and triethyl citrate were reacted with the chemical structure of rosin-based plasticizers. Rosin-based plasticizers with differently branched chains as alternative plasticizers for preparing phthalate-free flexible poly(vinyl chloride) films. All rosin-based plasticizers exhibited more excellent solvent extraction performance than phthalate plasticizers in four different solvents. The plasticizing efficiency of rosin-based plasticizers containing triethyl citrate groups reached 85.5%. The relationships between plasticizing efficiency, thermal stability, solvent resistance, tensile properties, and relative molecular mass of the branched chains of rosin-based plasticizers were investigated.

1. INTRODUCTION

Phthalates such as di-n-butyl phthalate, di(2-ethylhexyl)-phthalate, and di-n-octyl phthalate (DOP) are widely used in poly(vinyl chloride) (PVC) products such as food packaging materials, toys, and medical instruments.1 These synthetic organic chemicals are easily released from PVC products with increasing of time. Human reproductive and cardiovascular systems will be affected when people ingest or absorb the phthalates. Recently, some studies reported that the phthalates had a link with oxidative DNA damage,2 sex steroid hormones of children, and seminal plasma of reproductive-aged men.3–5 In order to decrease the potential threat of phthalates on people, many biomass resources have been used to produce plasticizers such as jatropha oil,6 glycerol,7 cardanol,8 lactic acid,9 and tung oil.10,11 In addition, the strategy of covalent attachment of different plasticizers onto a PVC matrix to obtain internally plasticized PVC materials was also reported.12–15

In recent years, the use of biomass resources has gained interest in producing plasticizers. Rosin is an important and renewable raw material in the chemical industry, which originates from pine trees. It is estimated that one million metric tons of rosin was produced in a year. The main component of rosin is rosin acid, which accounts for 90% of all components. Rosin can be used to synthesize many kinds of fine chemical products via the active groups such as the conjugated double bond and carboxyl acid.1,16 Rosin and its derivatives have served as alternatives to petrochemical products to produce cross-linking agents,17 biobased plastics and elastomers,18 epoxy resin,1 some polymers, and monomers.19 Dehydroabietaic acid (DA) is an important rosin derivative. The chemical structure of DA has the same benzene ring structure and a similar alkane structure compared with phthalate plasticizers; it is worth trying to synthesize different plasticizers using DA and combining with other renewable products such as castor oil methyl ester, cardanol, and triethyl citrate because these renewable products with special functional groups such as ester, benzene ring, and hydroxyl groups have been reported to synthesize plasticizers.20

In this study, three kinds of rosin-based plasticizers were designed and synthesized. First, DA was employed to react with oxalyl chloride to obtain chloride dehydroabietaic (CD); then, the obtained CD was used to react with cardanol, castor oil methyl ester, and tributyl citrate to produce rosin-based plasticizers with different branched chains. The synthesis...
route is showed in Figure 1. The obtained rosin-based plasticizers are with different branched chains and the same benzene rings and similar alkane structure compared to phthalate plasticizers. The chemical structures of all rosin-based plasticizers were characterized with $^1$H NMR and Fourier transform infrared (FT-IR). Plasticizing properties and solvent resistance of PVC films plasticized with different relative amounts of the rosin-based plasticizers were investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. Dichloromethane, oxalyl chloride, tetrahydrofuran (THF), methanol, potassium hydroxide, sodium hydroxide, petroleum ether, ethanol, DOP, acetic acid, pyridine, tributyl citrate, and castor oil were kindly provided by Nanjing Chemical Reagent Co., Ltd. All the raw materials were of analytical grade and used without further purification. DA (95%) was provided by Ta’ian Jia Ye Biological Technology Co. Ltd. Polyvinyl chloride (PVC) was supplied by Hanwha (South Korea). Cardanol (99%, acid value 5.5−6.6. Iodine value 210−250) was provided by Jining Hengtai Chemical Co., Ltd.

2.2. Synthesis of Castor Oil Methyl Ester. Castor oil methyl ester was synthesized and has been reported in our previous study.21

2.3. Synthesis of CD. DA (30 g, 0.10 mol) was dissolved in 60 mL of dichloromethane. Then, the mixture was put into a three-necked round-bottom flask with a reflux tube, thermometer, and gas conduit. Oxalyl chloride (17.64 g, 0.14 mol) was added in the mixture within 1 h at 0 °C. Then, the mixture was stirred at 30 °C for 4 h. The generated gas was introduced into the sodium hydroxide solution. CD was obtained after purifying by silica gel and vacuum distillation. CD was a yellow sticky liquid at 60 °C and white powder at 10 °C.

2.4. Synthesis of the End Group Cardanol−Rosin Ester Plasticizer. Pyridine (11 g, 0.14 mol), cardanol (42.56 g, 0.14 mol), and the obtained CD was dissolved in 80 mL of dichloromethane. The mixture was stirred at 30 °C for 6 h. Then, pyridine salt was filtered at 50 °C. Dichloromethane was removed by rotating evaporation. Unreacted cardanol and pyridine were removed by washing with methanol. Then, end group cardanol−rosin ester plasticizer (ECR) was obtained after purifying by silica gel and rotating evaporation.

2.5. Synthesis of the End Group Castor Oil Methyl Ester−Rosin Ester Plasticizer. Pyridine (11 g, 0.14 mol), castor oil methyl ester (43.68, 0.14 mol), and the obtained CD were dissolved in 80 mL of dichloromethane. The mixture was stirred at 50 °C for 6 h. Then, pyridine salt was filtered at 50 °C. Dichloromethane was removed by rotating evaporation. Unreacted castor oil methyl ester and pyridine were removed by washing with methanol. Then, the end group castor oil methyl ester−rosin ester plasticizer (ECMR) was obtained after purifying by silica gel and rotating evaporation.

2.6. Synthesis of the End Group Tributyl Citrate−Rosin Ester Plasticizer. Pyridine (11 g, 0.14 mol), tributyl citrate (38.64, 0.14 mol), and the obtained CD was dissolved in 80 mL of dichloromethane. The mixture was stirred at 50 °C for 6 h. Then, pyridine salt was filtered at 50 °C. Dichloromethane was removed by rotating evaporation. Unreacted tributyl citrate and pyridine were removed by washing with methanol. Then, the end group tributyl citrate−rosin ester plasticizer (ECTR) was obtained after purifying by silica gel and rotating evaporation.

2.7. Preparation of PVC Films. PVC and plasticizers were dissolved in 40 mL of THF according to the formulations in Table S1. The mixture was stirred at 50 °C for 20 min until the solution presented transparent. Then, the solution was poured into glass Petri dishes (10 cm diameter). PVC films were obtained after drying in a constant temperature drying box at 60 °C for 24 h to completely remove residual THF.

2.8. Characterizations. FT-IR spectra of rosin-based plasticizers and PVC films plasticized with different plasticizers were studied using a Nicolet iS10 FT-IR (Nicolet Instrument Corp., USA) Fourier transformed infrared spectrophotometer. FT-IR spectra were collected in the range of 4000−500 cm$^{-1}$. Infrared-characteristic absorption peaks were annotated using OMNIC software (Thermo Electron Corporation, USA).

$^1$H nuclear magnetic resonance (NMR) of rosin-based plasticizers were investigated on an AV-300 NMR spectrometer (Bruker Instrument Corp., Germany) at a frequency of 400
MHz. CDCl₃ was used as solvent and tetramethylsilane was used as an internal standard in the process. MestReNova software (Santiago de Compostela, Spain) was used to handle the NMR data.

Thermal stability of PVC films was investigated using a TG209F1 TGA thermal analysis instrument (Netzsch Instrument Corp., Germany) in N₂ atmosphere (50 mL/min). The heating rate was 10 °C/min. Thermal degradation data were collected from 40 to 600 °C.

The glass transition temperature (T_g) of PVC films was investigated using a NETZSCH differential scanning calorimeter (DSC) 200 PC analyzer under N₂ atmosphere. The temperature ranged from -20 to 100 °C at a heating of 20 °C/min. The DSC data were collected after removing thermal history. Five milligrams of PVC samples were weighed and sealed in a 40 μL aluminum crucible, and immediately tested using DSC measurement.

Tensile strength and elongation at break of all PVC films were detected according to GB/T 1040.1-2006 (China) at room temperature using an E43.104 Universal Testing Machine (MTS Instrument Corp., China). The strain rate was 10 mm/min and static tension was 50 N.

Solvent resistance of rosin-based plasticizers was investigated according to ASTM D5227. PVC films after weighing were immersed in distilled water, 10% (v/v) ethanol solution, 30% (w/v) acetic acid solution, and petroleum ether. The test condition was controlled at 23 ± 2 °C and the relative humidity was restricted at 50 ± 5%. After 24 h, the solvent-extracted PVC

Figure 2. (1) ¹H NMR spectra of DA. (2) ¹H NMR spectra of CD. (3) ¹H NMR spectra of ECMR. (4) ¹H NMR spectra of ECTR. (5) ¹H NMR spectra of ECR. (6) FT-IR spectra of rosin ester plasticizers.
films were dried and reweighed. The weight loss (WL) was calculated according to eq 1.

\[
WL = \left( \frac{W_i - W_f}{W_i} \right) \times 100
\]

where \( W_i \) was the initial weight of PVC films and \( W_f \) was the final weight of the test PVC films. The extraction loss data were collected using the average value of five test samples.

The solubility parameter of PVC and rosin-based plasticizers were investigated according to the Smalleq 2.25,26

\[
\delta = \sqrt{\text{CED}} = \sqrt{\sum F_i \frac{\Delta E}{V_i}} = \rho \sum F_i \frac{\Delta E}{M}
\]

where \( \delta \) = solubility parameter, CED = cohesive energy density, \( V_i \) = molar volume, \( \Delta E \) = energy of vaporization, and \( F_i \) = molar attraction constant. \( M \) = molecular weight and \( \rho \) = density of the plasticizers or chain unit of PVC. \( D \) = the difference of \( \delta \) between PVC and plasticizers.

The solubility parameter of PVC and rosin-based plasticizers were investigated according to the Small equation, eq 2.25,26

\[
\delta = \sqrt{\frac{\sum \Delta E \frac{1}{V_i}}{\sum \rho F_i \frac{\Delta E}{M}}}
\]

\[
D = \delta_{\text{PVC}} - \delta_{\text{plasticizer}}
\]

where \( \delta = \) solubility parameter, \( CED = \) cohesive energy density, \( V_i = \) molar volume, \( \Delta E = \) energy of vaporization, and \( F_i = \) molar attraction constant. \( M = \) molecular weight and \( \rho = \) density of the plasticizers or chain unit of PVC. \( D = \) the difference of \( \delta \) between PVC and plasticizers.

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The flexibility of PVC films was evaluated indirectly by calculating the plasticizing efficiency of rosin-based plasticizers based on the glass transition behaviors of PVC and PVC plasticized with rosin-based plasticizers. Plasticizing efficiency of rosin-based plasticizers was calculated using eq 4.27

\[
E_{\Delta T_g} \% = \frac{\Delta T_{g,\text{plasticizer}}}{\Delta T_{g,\text{DOP}}} \times 100
\]

where \( E_{\Delta T_g} = \) plasticizing efficiency of rosin-based plasticizers, \( \Delta T_g = \) the reduction in \( T_g \) from PVC to plasticized PVC films.

3. RESULTS AND DISCUSSION

The rosin-based plasticizers were characterized with \(^1\)H NMR and FT-IR, which are shown in Figure 2. In Figure 2(1), the multiple peaks at around 6.96–7.24 ppm are attributed to the protons of benzene rings.\(^{20}\) The signal at 2.85 ppm is attributed to protons of cycloparaffin. The peak at 2.20 ppm originates...
from the protons of methylidyne, which connects to the side chain of DA.28 The multiple peaks of protons of methyl appear at around 0.86−0.95 ppm.29 The signals at 1.2, 1.4, and 1.6 ppm are attributed to protons of other methylene groups. Figure 2(2) shows 1H NMR of CD; characteristic absorption peaks of CD do not present distinctly different compared to DA. However, compared to the FT-IR spectrum of DA and CD, as seen from Figure 2(6), the disappearance of hydroxyl groups at 3435 cm⁻¹ and the appearance of the strong signal of C−Cl at 735 cm⁻¹ in the FT-IR spectrum of CD indicate that CD was obtained. Figure 2(3) shows the 1H NMR of ECMR; the signals at around 5.35−5.61 ppm are protons of olefin, which originate from castor oil methyl ester.30 More signals corresponding to the protons of methylene appear at around 1.4−2.2 ppm compared to CD, which originated from castor oil methyl ester. Compared with the FT-IR spectrum of CD and ECMA, as seen from Figure 2(6), the signal at 1729 cm⁻¹, which is attributed to ester groups, becomes stronger than CD, and the signal attributed to C−Cl at 735 cm⁻¹ cannot be observed. Characteristic absorption peaks of double bonds appear at 3009 cm⁻¹, which is derived from castor oil methyl ester. These results indicated that ECMR was obtained. Figure 2(4) shows 1H NMR of ECTR; two strong signals at 4.2 and 3.9 ppm are attributed to protons of H₂C=CH₂−O− and −CH₂−C==O−, respectively.31 The peak at 1729 cm⁻¹ corresponding to ester groups is the strongest among the three kinds of rosin-based plasticizers in Figure 2(6), and the peak at 3735 cm⁻¹ attributed to C−Cl vanished. The 1H NMR of ECR is shown in Figure 2(5); the peaks at 5.0 and 5.5 ppm are assigned to protons of olefin, which originated from the long alkane chain of cardanol.31 The signals are the strongest among three kinds of rosin-based plasticizers, because there are more benzene rings in the chemical structure of ECR. In the FT-IR spectrum of ECR, the peak at 3007 cm⁻¹ is attributed to a double bond, which is derived from the long alkane chain of cardanol, and the peak at 735 cm⁻¹ corresponding to C−Cl vanished.24 Taken together, these results supported the conclusion that rosin-based plasticizers were obtained with well-designed molecular architectures.

The miscibility and plasticizing efficiency of the rosin-based plasticizers are evaluated via glass transition temperatures (T_g) through DSC and dynamic mechanical analysis (DMA) measurement. Figures 3 and 4d show DSC curves of PVC and plasticized PVC films. Figure 3 shows that there is one T_g for all plasticized PVC films, which indicates that PVC and rosin-based plasticizers are completely miscible. PVC has a T_g value of 85.6 °C. The T_g of plasticized PVC films decreases gradually with more rosin-based plasticizers added in PVC films, which indicates that rosin-based plasticizers decrease some of the intermolecular forces between PVC chains.32 The T_g for R4, MR4, and TR4 is 27.2, 37.2, and 14.2 °C, indicating that plasticizing efficiency of ECTR is the highest among the three kinds of rosin-based plasticizers. In order to prove the conclusion, the plasticizing efficiency of all rosin-based plasticizers was calculated according to eq 3. The plasticizing efficiency values are summarized in Table 1. The value for ECMR, ECR, and ECTR is 69.7, 57.8, and 85.5%, respectively. For rosin-based plasticizers, ECR with a rigid benzene ring structure has the lowest plasticizing efficiency, and ECTR with a high degree of branching has the highest plasticizing efficiency. DMA was also used to detect T_g of PVC materials, because DSC is less sensitive than DMA to detect T_g. The obtained...
DMA results are shown in Figure 4a–c. Only one tan δ peak of PVC and soft PVC materials can be observed in Figure 4a–c, which indicated that PVC and graft rosin-based plasticizers form a homogeneous mixture, and no free rosin-based plasticizers exists in the PVC matrix. These tan δ peaks correspond to Tg. The DMA results are basically consistent with DSC data.

The infrared absorption peak of carbonyl group of plasticizers will shift to a lower position when it was blended to PVC.33,34 The carbonyl group shifts that are larger in the plasticizers will shift to a lower position when it was blended with PVC. As seen from Figure 3d, the carbonyl group shifts of rosin-based plasticizers. For PVC plasticized with ECMR, the carbonyl group absorption peak shifts from 1730.6 to 1726.8 cm⁻¹. The order is the same with plasticizing efficiency Values of Rosin-Based Plasticizers.

|                | ECMR | ECR | ECTR |
|----------------|------|-----|------|
| E sóc (%)      | 69.7 | 57.8| 85.5 |

Figure 5 presents the tensile test results. As we concluded, ECTR has the highest plasticizing efficiency among the three kinds of rosin-based plasticizers based on DSC, DMA, and FT-IR. As seen from Figure 5, the tensile strength of all PVC films decreases gradually with more rosin-based plasticizers blending with PVC, and the elongation at break of all PVC films increases gradually. The addition of rosin-based plasticizers decreases the entanglement of PVC chains. PVC materials become flexible when rosin based plasticizers are blended with the PVC. However, rosin-based plasticizers present different plasticizing efficiencies. For ECMR, elongation at break increases from 180 to 307%. The value for ECR is from 180 to 279%. ECTR shows the best elongation at break, which increases from 108 to 346%. Tensile strength for ECMR, ECR, and ECTR decreases from 30 to 12.5, 15.7, and 8.1 MPa, respectively. At the same weight ratio, ECTR gives the best plasticizing efficiency. The conclusion is consistent with the DSC, FT-IR, and theory based on the chemical structure of rosin-based plasticizers.

Thermal degradation of plasticized PVC films has been investigated. As seen from Figure 6, thermal degradation processes of all PVC films have two stages; the first stage is at around 260–350 °C, which is attributed to pyrolysis of PVC dechlorination. The second stage at around 400–540 °C is due to the destruction of chains and forms cross-linking, cyclization, and cleavage compounds.38 TGA data of all PVC films are summarized in Table S2. These data include the 5% weight loss temperature (T5), the 50% weight loss temperature, char residue, weight loss at around 260–350 °C, and weight loss at around 400–540 °C. As seen from Table S2, for PVC films plasticized with ECMR, the thermal stability of PVC films decreases with more ECMR blending with PVC. T5 decreases from 276.5 to 265.0 °C, and T50 decreases from 344.6 to 322.7 °C. Because the thermal stability of ECMR is poor at above 250 °C, benzene rings of ECMR are thermally degraded completely. The weight loss of PVC at around 260–350 °C is 62.5%, but the value for MR4 is down to 41.2%. On the contrary, the weight loss at around 400–540 °C increases from 27.2 to 32.05%. The weight loss at around 400–540 °C originates from thermal degradation of ECMR. The branched chain of the ECMR (castor oil methyl ester), which is derived from castor oil, degrades rapidly at above 367 °C. Then, thermal degradation of MR4 produced more char residue than PVC. For ECR, the thermal degradation process of PVC films shows the same trend compared with MR films. T5 and T50 decrease from 276.5 and 344.6 to 252.8 and 325.1 °C, respectively. Thermal degradation of benzene rings in the ECR occurs at this temperature range. Weight loss of R4 at 260–350 °C is down to 40.2%. On the contrary, weight loss at around 400–540 °C increases from 27.2 to 30.0%, which is attributed to thermal degradation of ECR, because double bonds in the alkyl chain of the cardanol group of ECR are thermally unstable, which is converted into more stable epoxides at above 260–350 °C, and thermal degradation occurs at around 400–540 °C. The char residue produced by R4 is 13.05%, which is more than that of PVC (5.8%). The thermal degradation process of TR films presents a different...
trend compared with MR films and R films. $T_5$ and $T_{50}$ are down to 173.2 and 322.6 °C, weight loss of TR4 at 260−350 °C is down to 40.7%, but weight loss at around 400−540 °C is little changed; the value is around 25.2% because ECTR is almost in complete thermal degradation at 400 °C.

Migration behavior was investigated by evaluating the weight loss of PVC films in four different solvents [distilled water, 10% (v/v) ethanol solution, 30% (w/v) acetic acid solution, and petroleum ether], which was designed according to the environments where plasticized PVC materials are used. The excellent solvent resistance of plasticizers can keep properties of plastic products long stable. Solvent resistance results of rosin-based plasticizers are showed in Figure 6. DOP presents the poorest solvent resistance among the four different plasticizers in four different solvents. The most weight loss of PVC-D is in petroleum ether; the value is 12.3%, whereas PVC-D only lost 1.8% of its weight in distilled water. For PVC films plasticized with rosin-based plasticizers, weight loss increases in four solvents with more rosin-based plasticizers blending with PVC. However, the three kinds of rosin-based plasticizers show better solvent resistance than DOP. For ECR, R4 lost 1.4, 7.0, 3.2, and 2.7% of its weight in distilled water, petroleum ether, 10% (v/v) ethanol, and 30% (w/v) acetic acid, respectively. Weight loss for MR4 in distilled water, petroleum ether, 10% (v/v) ethanol, and 30% (w/v) acetic acid is 1.2, 5.0, 2.2, and 2.3%, which indicates that solvent resistance of ECMR is better than that of ECR. TR4 lost the most weight among the three kinds of PVC films; the weight loss for TR4 is 1.3, 7.6, 6.1, and 3%, respectively, which illustrated that solvent resistance of ECTR is worse than that of ECR and ECMR. On the basis of these results, we can conclude that the plasticizer with lower molecular weight may have poor solvent resistance, because the order of molecular weight for DOP and rosin-based plasticizers is DOP (390) < ECTR (574) < ECR (602) < ECMR (612).

Solubility parameter ($\delta$) is an important value to evaluate the compatibility between polymers and plasticizers. Polymers can be well dissolved in plasticizers when $\delta$ of the polymers and the plasticizers is the same or the difference is less than $\pm 3.07$ (J/cm$^3$)$^{1/2}$. The $\delta$ value and the difference of $\delta$ between PVC
and plasticizer \((D)\) for PVC, DOP, and rosin-based plasticizers was calculated according to eqs 2 and 3, and compared in Table 2. The obtained \(\delta\) of ECR, ECMR, and ECTR is 7.71 (J/cm\(^3\))\(^{1/2}\), 7.50 (J/cm\(^3\))\(^{1/2}\), and 8.46 (J/cm\(^3\))\(^{1/2}\), respectively. The \(D\) value for ECTR [1.20 (J/cm\(^3\))\(^{1/2}\)] is the least among the three kinds of rosin-based plasticizers, but is greater than DOP [0.77 (J/cm\(^3\))\(^{1/2}\)], illustrating that compatibility between ECTR and PVC is better than that of ECR and ECMR, but worse than that of DOP. The order of compatibility is DOP > ECTR > ECR > ECMR; the results are consistent with previous results of DSC, FT-IR, and tensile tests.

Free volume theory is used to explain why the \(T_g\) of the polymer decreases when the plasticizer is blended with the polymer. It was noted that the specific volume of the polymer decreased when temperature was down until it reached \(T_g\); then, the specific volume almost kept unchanged, and free volume caused the increase of specific volume above \(T_g\)\(^{42-44}\). Pure PVC presents hard and rigid, because pure PVC chains are tangled together and have strong intermolecular force \(F'\) between the chains, there is not any free volume existed in PVC matrix. The addition of plasticizers increase the distance of PVC chains and decrease the intermolecular force \(F''\), then produce free volume between polymer and plasticizer. In this study, the plasticizing mechanism of rosin-based plasticizers according to free volume theory can be observed in Figure 7e,f; the addition of rosin-based plasticizers increases the free volume of PVC chains and promotes the PVC chains to move. The behavior decreases tensile strength and increases elongation at break of PVC films. However, DOP and rosin-based plasticizers showed different plasticizing efficiencies, because DOP and ECTR with smaller relative molecular mass and relatively more carbonyl group, electron cloud on benzene rings, and oxygen atoms than ECR and ECMR increase \(F''\) and decrease \(F'\), thus presenting a higher plasticizing efficiency than ECR and ECMR.

The plasticizing mechanism of rosin-based plasticizers can be explained according to mathematical models for plasticization, which was reported by Mauritz and Storey\(^{42,45}\). In the theory, the decrease of \(T_g\) was caused by branched chain movement. The same molecular mass plasticizers with a higher branched chain will provide more excellent plasticizing properties than linear plasticizers\(^{37}\). In this study, molecular structure DOP and ECTR have higher branched chains than ECR and ECMR, as seen from Figure 7a−d, which was more effective to reduce the \(T_g\) of PVC films, thus giving a higher plasticizing efficiency. In addition, the long branched chain of ECR and ECMR may

### Table 2. Solubility Parameter of PVC, DOP, and Rosin-Based Plasticizers

| Items      | \(\delta\) (J/cm\(^3\))\(^{1/2}\) | \(D\) (J/cm\(^3\))\(^{1/2}\) |
|------------|----------------------------------|--------------------------------|
| PVC        | 9.66                             |                                |
| DOP        | 8.59                             | 0.77                           |
| ECR        | 7.71                             | 1.95                           |
| ECMR       | 7.50                             | 2.16                           |
| ECTR       | 8.46                             | 1.20                           |

Figure 7. Plasticizing mechanism of rosin-based plasticizers according to free volume theory and lubricity theory. (a−d) Branched chains’ movement and electron cloud distribution of ECMR, ECTR, ECR, and DOP; (e,f) force between PVC molecules and plasticizer molecules.
tangle with PVC and produce an anti-plasticization effect on PVC films.

Lubricity theory holds that plasticizers play the role of lubrication and improve the movement of PVC chains in plasticized PVC materials. As seen from Figure 7ef, surface irregularities and internal entanglement of PVC prevent PVC chains from moving freely. Rosin-based plasticizers were used to dissolve PVC chains as solvents, which made PVC chains move freely by decreasing the F’. DOP and ECTR dissolve PVC more easily because F” was stronger than ECR and ECMR, thus producing a higher plasticizing efficiency.

4. CONCLUSIONS
In conclusion, we developed three kinds of rosin-based plasticizers with differently branched chains as alternative plasticizers for preparing flexible PVC films. The plasticizing efficiency value for ECMR, ECR, and ECTR was 69.7, 57.8, and 85.5%, respectively. Rosin-based plasticizers with rigid benzene rings and long alkane chains had a negative impact on plasticizing efficiency and miscibility; the carbonyl groups of rosin-based plasticizers were responsible for plasticizing efficiency and miscibility. At the same weight ratio, ECTR gave the best plasticizing efficiency among the three kinds of rosin-based plasticizers. The order of solvent resistance for DOP and rosin-based plasticizers is DOP (M_w = 390) < ECTR (M_w = 574) < ECR (M_w = 602) < ECMR (M_w = 612); the order of compatibility between PVC and plasticizers is DOP > ECTR > ECR > ECMR, illustrating that relative molecular mass of plasticizers is closely related with solvent resistance and compatibility.

■ ASSOCIATED CONTENT

Supporting Information
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Formulations of PVC and plasticized PVC films; TGA and DSC data of PVC films (PDF)

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