Effect of Modified Cardanol as Secondary Plasticizer on Thermal and Mechanical Properties of Soft Polyvinyl Chloride

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**ABSTRACT:** This study represents the first attempt to prepare a novel cardanol-based plasticizer. Modified cardanol (MC, i.e., phosphorylated cardanol) containing nitrogen and phosphoric acid groups was synthesized and then incorporated into polyvinyl chloride (PVC) as the secondary plasticizer for partial substitution of dioctyl phthalate (DOP). The molecular structure of MC was characterized by Fourier transform infrared spectroscopy, $^1$H nuclear magnetic resonance (NMR), and $^{31}$P NMR spectroscopy. The thermal degradation behavior, mechanical performance, and compatibility of MC were also investigated. The substitution of DOP with MC enables PVC blends to have higher thermal stability, tensile strength, and leaching resistance. The tensile strength is increased from 17.7 MPa for DOP/PVC blend (MC-0) to 25.7 MPa for MC/PVC blend (MC-4), and the elongation at break is increased from 256 to 432%, respectively. The microstructure of the tensile fractured surface was studied by scanning electron microscopy. The results show that the addition of MC allows PVC blends to have well-balanced properties of flexibility and strength and excellent migration resistance.

**INTRODUCTION**

Polyvinyl chloride (PVC) has extensive industrial and domestic applications, and PVC products have infiltrated the market, once dominated by metal products, with an annual growth rate of over 5.9%. The versatile nature of PVC makes it an appealing material in many industries such as building, packaging, daily consumable goods, electronics, and toys. However, the commercial application of PVC may be limited because of its brittleness and low thermal stability. In order to overcome such limitations, PVC is blended with various plasticizers to enhance its thermal stability and flexibility. Obviously, these plasticizers are technically and economically important in the plastic industry. Phthalate esters are the most commonly used plasticizers. For example, dioctyl phthalate (DOP) has been widely used in children articles, packaging and wire insulation materials, syringes, blood transfusion tubes, and IV bags. However, concerns have been expressed about the leaching and poor mechanical properties of DOP as a plasticizer, which may reduce the shelf and service lives of PVC products and cause endocrine malfunctioning and potential carcinogenic activity.

Given the adverse effects of DOP and depletion of petroleum resources, biobased plasticizers have attracted growing academic and industrial interests, including vegetable oils, succinic acid, citric acid, fatty acid, and isosorbide. However, these plasticizers also have some drawbacks that need to be addressed, such as low compatibility with PVC, low plasticization efficiency and poor heat stability due to the aliphatic structure, and higher molar mass compared to phthalate plasticizers. Among renewable plasticizers, phosphorus-containing bioplastics can enhance the thermal stability, and the aromatic group in bioplastics can improve the compatibility of the plasticizer with PVC. The biobased cardanol oil isolated from cashew nut shell liquid can act as an epoxy curing agent and as a plasticizer. The use of cardanol as the primary or secondary plasticizer can enhance the flexibility and thermal stability and decrease the volatility of PVC materials. It has also been suggested that some renewable plasticizers have good leaching resistance, plasticization efficiency, and excellent thermal stability.

Therefore, this study aims to modify cardanol to prepare a biobased plasticizer to improve the plasticization efficiency, mechanical property, and thermal stability. The Mannich base of cardanol was phosphorylated using a low cost, environmentally friendly method and employed as a secondary plasticizer for partial substitution of DOP. The synthesized plasticizer [modified cardanol (MC), i.e., phosphorylated cardanol] was characterized by Fourier transform infrared spectroscopy.
(FTIR), proton NMR (1H NMR), phosphorus NMR (31P NMR), and energy-dispersive X-ray (EDX) spectroscopies. The mechanical and thermal characteristics, loss modulus, and leaching stability of the MC/PVC blends were evaluated. The plasticizing and leaching effects of MC in PVC blends as a secondary plasticizer were also determined and compared with DOP.

### RESULTS AND DISCUSSION

#### Structural Characterization of MC

The structure of MC was characterized by FTIR, NMR, EDX, and thermal gravimetric analysis (TGA). The FTIR spectra of the Mannich base of cardanol and MC are shown in Figure 1. The Mannich base of cardanol shows a characteristic band at around 1270 cm\(^{-1}\), which is assigned to the stretching of the −C–N− bond. Other absorption bands can be due to the −C=−C− (1587 cm\(^{-1}\)), −Ar (aromatic) (1619 cm\(^{-1}\)), −CH\(_2\)− (2836 cm\(^{-1}\)), −CH\(_3\) (2925 cm\(^{-1}\)), and alkene (3008 cm\(^{-1}\)) stretching vibrations. The absorption band at 3200−3300 cm\(^{-1}\) corresponds to −N–H stretching vibrations of primary and secondary amines. These results indicate the occurrence of the Mannich reaction. After phosphorylation of the Mannich base of cardanol, new peaks appear in the FTIR spectra of MC, which confirms the successful phosphorylation. The new peaks at 1040, 1170, and 1240 cm\(^{-1}\) are attributed to P=O and P−O stretching vibrations. The broad bands of −OH of O=PO−OH (2200 cm\(^{-1}\)) and −OH (3400 cm\(^{-1}\)) are also observed.

1H NMR and 31P NMR spectroscopies were performed to validate the successful synthesis of MC, as shown in Figure 2. In the 1H NMR spectrum of MC (Figure 2a), the chemical shift in the range of 6.5−7.0 ppm is assigned to the aromatic protons (label 1), whereas that in the range of 5.8−6.5 ppm is assigned to the protons (label 11) of the triene, diene, and monoene moieties. The chemical shift in the range of 5.0−5.5 ppm is assigned to −NH− and −OH protons (labels 4 and 2). The chemical shift of protons adjacent to the nitrogen moiety is observed at 2.5 ppm and 3.2 ppm (labels 5 and 3). The chemical shift at 1.2, 1.4, and 2.8 ppm is attributed to the methylene groups (label 7, 10, and 12) from the long side chain of the cardanol unit, whereas that at 0.7 ppm is attributed to the terminal methyl groups of dienes, monoene, and penta decyl moieties (label 13). The 31P NMR spectrum of MC (Figure 2b) shows a chemical shift at 0.92 ppm, which is attributed to the phosphorous atoms originating from the phosphoric acid moiety. These results confirm the successful synthesis of MC, which is consistent with the proposed chemical structure.

Figure 3 shows the EDX spectra of the Mannich base of cardanol and MC, and the atomic weight percentages of elements are summarized in Table 1. The EDX results of MC reveal the successful phosphorylation of the Mannich base of cardanol. The Mannich base of cardanol contains 82.94 at. % carbon, 7.28 at. % nitrogen, and 9.78 at. % oxygen, but no phosphorus is present in this sample. However, after phosphorylation, MC contains 64.15 at. % carbon, 8.56 at. % nitrogen, 24.53 at. % oxygen, and 2.75 at. % phosphorus. The reason for the reduction in the carbon content of MC is that its surface is hindered by the phosphoric acid moiety. However, there is a negligible change in the nitrogen content. The increase in the oxygen content of MC is due to the oxygen of the phosphoric acid moiety, and the presence of 2.75 at. % phosphorus confirms the successful phosphorylation.

#### TGA Results

The thermal stability of plasticizers and blends was determined by TGA (Figure 4a). Table 2 summarizes the thermal characteristics of these two plasticizers and PVC blends, including 5 (T\(_{10}\)), 10 (T\(_{15}\)), and 50 (T\(_{50}\)) percent weight loss temperatures and residues. MC shows 5% weight loss at 237.8 °C (Figure 4a), with an increment of 33.6 °C, in comparison with that of DOP (204.2 °C). At 600 °C, there is 0.1 and 25.9% of residue for DOP and MC, respectively. So, it can be inferred that the high thermal stability of MC is due to the phosphoric acid, benzene, and nitrogen moiety of MC.

The TGA curves for blends with different MC contents are presented in Figure 4b. A two-stage thermal degradation pattern is observed in all blends. A 60% mass loss is observed at 220−360 °C, followed by 20% mass loss at 400−510 °C because of the degradation of PVC blends. The TGA curves demonstrate that the T\(_{10}\) and T\(_{50}\) values of PVC blends are enhanced with the substitution of DOP with MC. For instance, at 600 °C, the residue of MC-0 is 7.1%, and increasing the MC...
content from 2 to 10 phr leads to an increase in the char residue from 8.1 to 17.4%. These results indicate that the increase in char may account for the improvement of the thermal stability of PVC blends. Hence, MC is more efficient than DOP in improving the thermal stability of PVC blends.

Microstructure. The morphology of the fractured surfaces of the blends obtained from tensile tests was determined by scanning electron microscopy (SEM) (Figure 5). Shallow ridges and cracks are observed in MC-0, which may be responsible for the elongation at break and the lower tensile strength (Figure 5a). However, the addition of MC leads to significant changes in microstructures. For instance, deep oriented ridges can be seen in the fractured surface of MC-1 and MC-2 (Figure 5b,c), indicating intensified plastic deformation which is responsible for the high elongation at break for MC-1.37,38 Increasing the MC content contributes to the deformation of the fractured surface of both MC-3 and MC-4 (Figure 5d,e). MC-3 has smooth and homogenous deformation and ridges on the fractured surface, but the deformity increases in MC-4, which indicates high tensile strength and break resistivity.

Mechanical Properties. PVC is brittle, but the addition of a plasticizer can make PVC become soft and moldable by increasing the motion of PVC molecules.39 Therefore, it is crucial to optimize the formulation of plasticizers to boost the performance of PVC blends. The tensile strength and elongation at break of the blends are shown in Table 3. MC-0 has a tensile strength of 17.7 MPa, and increasing the MC content from 2 to 10 phr results in an enhancement in tensile strength from 23.5 to 25.7 MPa. This is associated with the presence of rigid groups (aromatic, hydroxyl, nitrogen, and phosphoric acid), which can restrict the movement of the polymer chain via molecular interactions and thus enhance the tensile strength of blends.40,41 The flexibility of MC-1 to MC-4 (536−432%) is higher than that of MC-0 (256%) because of the alkyl chain of MC, which provides shielding effect and lubricity to the polymer chain.41−43 Increasing the MC content in MC/PVC blends results in an increase of rigid groups (aromatic, hydroxyl, nitrogen, and phosphoric acid) and thus enhanced interactions with the PVC matrix, which can restrict the polymer chain motion and consequently lead to low flexibility.40,41

Dynamic Mechanical Analysis Results. The dynamic mechanical behaviors of blends were characterized in order to evaluate the effect of plasticizer (MC) on the PVC matrix, as shown in Figure 6. The glass transition temperature $T_g$ is used to indicate the efficiency of the plasticizer. Figure 6 indicates that all blends show a single $T_g$ revealing that the

| Table 1. Atomic Composition of Different Elements in the Mannich Base of Cardanol and MC |
| --- |
| serial # | C | N | O | P |
| Mannich base of cardanol | 82.94 | 7.28 | 9.78 |  |
| MC | 64.15 | 8.56 | 24.53 | 2.75 |

| Table 2. TGA of MC/PVC/DOP Blends |
| --- |
| sample | $T_g$ (°C) | $T_{50}$ (°C) | $T_{50}$ (°C) | residue (%) (at 600 °C) |
| DOP | 204.2 | 226.5 | 339.1 | 0.1 |
| MC | 237.8 | 272.7 | 443.5 | 25.9 |
| MC-0 | 235.2 | 245.2 | 275.2 | 7.1 |
| MC-1 | 239.1 | 246.5 | 281.6 | 8.1 |
| MC-2 | 241.5 | 249.1 | 284.1 | 10.5 |
| MC-3 | 250.6 | 262.6 | 290.1 | 15.1 |
| MC-4 | 251.8 | 264.3 | 294.3 | 17.4 |

Figure 3. EDX results of the Mannich base of cardanol (a) and MC (b).

Figure 4. TGA curves of MC, DOP (a), and plasticized PVC blends (b).
plasticizer has excellent compatibility with PVC.44 Table 2 shows that the \( T_g \) value first decreases from 1 °C (MC-0) to −5 °C (MC-1) when DOP is substituted with 2 phr MC (MC-1) and then increases to −1 °C (MC-2) when DOP is replaced with 5 phr MC (MC-2). The increase in the content of MC also increases the number of polar groups (e.g., hydroxyl, nitrogen, and phosphorus acid) and alkyl chains. The polar groups restrict the movement of PVC chains, leading to an increase in the mechanical strength and plasticizer compatibility with PVC.45,46 However, with the further increase in the MC content from 7 to 10 phr, the \( T_g \) values of MC-3 and MC-4 are higher than that of MC-0, which can be attributed to the restriction of PVC polymer chain movement with increasing plasticizer polar groups. Therefore, the mechanical strength of MC-3 and MC-4 increases, but the elongation at break slightly decreases. The results suggest that the presence of MC can significantly enhance the tensile properties of MC/PVC blends because of excellent compatibility between plasticizers and PVC.

**Migration Tests.** The migration of the plasticizer is indicated by the quantity of plasticizers leached from the PVC blends to exudation (solid), extraction (liquids), and volatility (air).44 The leaching of plasticizers from PVC blends can critically affect their compatibility with PVC, which can be affected by the plasticizer structure, polarity, temperature, and surrounding media.45,47 However, many factors should be taken into account in evaluating the plasticizer migration.48 In general, the most important factors are the structure and compatibility of the plasticizer with PVC. The leaching of the plasticizer from PVC blends in distilled water, petroleum ether (p-ether), and \( n \)-hexane is evaluated (Figure 7a). The solubility profile of \( n \)-hexane is similar to that of cooking oil, and hence it is used as an extraction medium.49 It is observed that the PVC blends (MC-0 to MC-4) display lower extraction resistance in \( n \)-hexane and p-ether than in distilled water, which may be attributed to the organic nature of the plasticizer.

Interestingly, the leaching of the plasticizer decreases with the substitution of DOP with MC in \( n \)-hexane and p-ether solvents. For instance, the weight loss of MC-0 in p-ether (12.6%) and \( n \)-hexane (10.1%) is about 6 times higher than that of MC-4 (2.6% in p-ether and 3.5% in \( n \)-hexane). The extraction of MC-4 can be restricted by the phosphoric acid and nitrogen groups of MC, which can form a strong interaction with PVC chains. The interaction bridge between DOP and PVC matrix because of the presence of MC can also reduce DOP extraction, and this trend is consistently observed in the PVC blends (Figure 7a), indicating that the extraction stability mainly depends on the polarity and high molecular weight of plasticizers.50 MC-1 to MC-4 blends exhibit better
exudation resistance than MC-0 (Figure 7b), which indicates that the MC plasticizer shows excellent compatibility with the PVC matrix. A similar trend is also observed in the volatility (Figure 7b) of plasticizers. These findings suggest that the volatility of the plasticizer can be enhanced by substituting DOP with MC. Thus, the high migration resistance of MC may enhance the longevity of PVC blends and the compatibility of DOP with PVC.

**CONCLUSIONS**

A novel cardanol-based plasticizer was synthesized in this study and then incorporated into PVC to improve the thermal, mechanical, and leaching stabilities. For this purpose, a commercially available plasticizer was partially substituted with MC. The thermal stability of PVC blends is increased significantly as the MC content increases. The soft PVC obtained with MC as the secondary plasticizer shows higher tensile strength (25.7 MPa) and elongation at break (432%) compared with the neat DOP/PVC blend. The addition of MC allows the PVC blend to have well-balanced flexibility and strength. The dynamic mechanical analysis (DMA) result indicates that the addition of 2–5 phr of MC has excellent plasticizing effects on PVC blends compared with DOP. Plasticizer migration tests reveal that the leaching resistance of MC is 6 times higher than that of DOP, suggesting better compatibility of MC with PVC. This study may provide important insights into the synthesis of cardanol-based secondary plasticizers to improve the mechanical, thermal, and migration stabilities of PVC.

**EXPERIMENTAL SECTION**

**Materials.** Cardanol was obtained from Cardolite Chemical (Zhuhai, China). Tetrahydrofuran (THF 99%), ethanol (99%), phosphoric acid, paraformaldehyde, DOP (99.5%), diethylenetriamine (>97%), p-ether, and n-hexane were supplied by Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). PVC (S-1000) was purchased from Sinopec Qilu Co. Ltd. (Zibo, China). Calcium stearate and zinc stearate were supplied by Changzhou Huaren Chemical Co. Ltd. (Changzhou, China). Deionized water was used throughout the experiments.

**Methodology.** Synthesis of Mannich Base of Cardanol. The Mannich base of cardanol was synthesized as described previously. Cardanol (5 mmol) was charged into a 500 mL three-necked flask; then diethylenetriamine (5 mmol) was added and refluxed at 60 °C with stirring for 30 min; and then paraformaldehyde (5 mmol) was added in portions. When paraformaldehyde was dissolved completely, the temperature of the mixture was increased to 80 °C and kept at that temperature for 3 h. Then, the residual reactants were removed under vacuum at 80 °C for 1 h to yield the product. The yield of Mannich base of cardanol was 93.4%.

**Synthesis of MC.** The Mannich base of cardanol was phosphorylated as follows. Phosphoric acid (1 mol) and paraformaldehyde (1 mol) were simultaneously added into the Mannich base of cardanol (1 mol) at 70 °C and refluxed for 3 h in a three-necked flask. The resultant MC was washed three times with deionized water and then dried in a rotary evaporator at 100 °C for 2 h. The yield of MC was 91.0%.

**Preparation of Plasticized PVC Blends.** A set of plasticized PVC blends were prepared, as shown in Table 4. PVC powder, plasticizers, and thermal stabilizers (Ca soap/Zn soap = 3:1) were blended at room temperature for 5 min, heated to 160 °C for 10 min using a double-roller blender (Zheng Gong Co., China), and squeezed into thin sheets of 2 mm (see Figure S2).

**Characterization and Measurements.** The FTIR spectra were measured at a scan rate of 4 cm⁻¹ ranging from 400 to 3900 cm⁻¹ at room temperature using a Nicolet 6700 spectrometer in the transmittance mode.
The $^1$H and $^{31}$P NMR spectra of MC dissolved in deuterated THF were recorded using a Bruker 400 MHz spectrometer (Bruker, Rheinstetten, Germany) at room temperature.

TGA was conducted with a TA 50 thermogravimetric analyzer under a $N_2$ atmosphere at a rate of $10\, ^\circ\text{C}\, \text{min}^{-1}$ from 40 to 600 $^\circ\text{C}$.

The tensile fracture morphologies of the PVC blends were observed by SEM (FE-S4800, Hitachi). Before the analysis, a layer of gold was vacuum-sputtered on all samples.

The mechanical properties of the blends were measured according to the Chinese standard GB.T.1040.3 with a cross-head speed of 10 mm/min at room temperature using a MTS E43 universal testing machine. All specimens were conditioned at 23 $^\circ\text{C}$ for 1 day before testing. The average of six measurements was reported for each blend.

DMA was performed using a DMA Q800 analyzer in the dual cantilever mode with a frequency of 1 Hz. The testing temperature swept from $-60$ to $100\, ^\circ\text{C}$ at a heating rate of 3 $^\circ\text{C}\, \text{min}^{-1}$. To assure reproducibility of the data, tests were replicated for each specimen.

For exudation, the PVC blend was sandwiched between two pieces of filter paper and then placed into the oven at 70 $^\circ\text{C}$ for 48 h. After that, the exudation was calculated by measuring the weight loss of the sample using eq 1. Three samples were tested to obtain an average value.

Weight loss (%) $= \frac{W_i - W_f}{W_i} \times 100$ (1)

where $W_i$ and $W_f$ are the sample weights before and after the test, respectively.

In volatility tests (ISO 176:2005), the samples were positioned at the center of activated carbon in a Petri dish and then placed in the oven and air circulated at 70 $^\circ\text{C}$ for 24 h. After that, the samples were brushed clean from the activated carbon residue, and the weight loss was calculated according to eq 1.

In the extractability tests (ASTM 1239-98), samples were submerged in p-ether, n-hexane, and deionized water at room temperature for 24 h. After that, they were dried at 30 $^\circ\text{C}$ for 24 h, and the weight loss was calculated according to eq 1.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00826.

Pictures of modified cardanol and plasticized PVC samples (PDF)

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### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This research is financially supported by the National Natural Science Foundation of China (21764011), the Foundation from Qinghai Science and Technology Department (2020-HZ-808), the Kunlun Scholar Award Program of Qinghai Province, and the Thousand Talents Program of Qinghai Province.

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