



PVC materials without migration obtained by chemical modification of azide-functionalized PVC and triethyl citrate plasticizer



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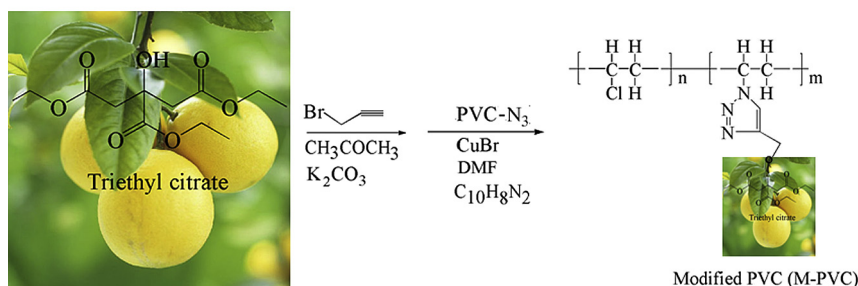
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HIGHLIGHTS

- PVC materials were modified with bio-based triethyl citrate.
- Modified PVC materials exhibited near-zero migration in four different solvent.
- Modified PVC materials have potential application in durable plastic products.

GRAPHICAL ABSTRACT



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ABSTRACT

In the study, PVC material modified with bio-based triethyl citrate plasticizer was synthesized. PVC was first reacted with sodium azide in order to get the azide-functionalized PVC (PVC-N₃). Then the modified PVC material (M-PVC) was prepared by the reaction of PVC-N₃ and propargyl ether triethyl citrate. The PVC material was characterized with FT-IR, H¹ NMR, elemental analysis, GPC, TGA and DSC. The obtained M-PVC material has higher thermal stability and lower glass-transition temperature compared to plasticized PVC with dioctyl phthalate (DOP). It exhibited near-zero migration in four different solvents (distilled water, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether). The method provides general method for efficient use of biomass resources based plasticizer.

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1. Introduction

PVC is the third most widely produced polymer in the world, with its excellent mechanical strength, thermal stability, flame retardancy and insulation characteristics, has been widely used as a high performance resin in many products such as in food

packaging, pipes, toys, medical devices, wire and cable [1,2]. Unfortunately, pure PVC is so brittle cannot be processed for extrusion molding to obtain consumer products. PVC is usually mixed with amounts of plasticizers, up to 70% by weight [3]. PVC products account for approximately 80% of all types of plasticizers consumed in China [4]. Dioctyl phthalate (DOP) and dibutyl phthalate (DBP), as the main commercial plasticizers easily migrate into surrounding and reduce performance of PVC products. The loss of plasticizer cannot maintained the properties of the PVC products long stable, as well as potential toxicity to human body [5–12]. Many alternatives to phthalate plasticizers have been explored. Hundreds of non-toxic plasticizer derived from renewable resources have been developed or used as commercial plasticizer such as cardanol-based plasticizer [13], epoxidized sunflower oil [14], epoxidized safflower oil [15], glycerol esters [16], rice fatty acid [1], triethyl citrate [17], citric acid [18] and acetyl tri-n-butyl citrate [19]. However, all of these plasticizers is external plasticizer; migration can not be avoided with the increasing of time. The use of internal plasticizers can avoid migration of plasticizer from PVC matrix, because internal plasticizers are the parts of the polymer matrix [20]. Internal plasticizers can be prepared via chemical modification of polymer matrix. Recently, Ddina et al. synthesized the full-erated PVC by the chemical reaction of azido-functional PVC with C₆₀. [21] The obtained PVC materials retained the electronic properties of C₆₀, and the processability of PVC was maintained [22]. Lafarge et al. developed new bacteria repellent PVC materials by chemical synthesis with bioactive polysaccharides and PVC materials [23]. Kiskan et al. studied novel side-chain benzoxazine functional polyvinylchloride (PVC-Benzoxazine) [24]. The obtained PVC materials presented more thermal stable than that of pure PVC. In addition, macromolecular photoinitiators [25], antimicrobial aliphatic copolyester [26], one component polymeric photoinitiator [27], polymeric architectures [28], degradable model networks and functional telechelics [29,30] were also prepared with chemical modification of PVC.

In the present work, the modified PVC (M-PVC) material was prepared by the addition of propargyl ether bio-based triethyl citrate onto azide-functionalized PVC (PVC-N₃). The final product was expected to retain the near-zero migration. The chemical structure, molecular mass and thermal properties were investigated. Also, the degree of migration of M-PVC in four different solvents (distilled water, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether) was examined. The method provides general method for efficient use of biomass resources based plasticizer.

2. Experimental section

2.1. Materials

Triethyl citrate, propargyl bromide solution, potassium carbonate, sodium azide, *N,N*-dimethylformamide (DMF), methanol, acetone, cuprous bromide, 5,5-dimethyl-2,2-dipyridyl and dioctyl phthalate (DOP) were kindly provided by Nanjing Chemical Reagent Co., Ltd. Polyvinyl chloride (PVC) was supplied by Hanwha (South Korea).

2.2. Synthesis of propargyl ether triethyl citrate

Propargyl ether triethyl citrate was prepared by dissolving 13.8 g (50 mmol) of triethyl citrate, 6.54 g (55 mmol) of propargyl bromide solution, 7.6 g (55 mmol) of potassium carbonate in 30 mL of acetone. The mixture was stirred at 65 °C for 12 h. Then the mixture was washed with deionized water three times. The solution was purified by evaporating under vacuum. Fig. 1 showed the synthetic route of propargyl ether triethyl citrate (Yield:97%).

2.3. Synthesis of azide-functionalized PVC (PVC-N₃)

PVC-N₃ was prepared by dissolving 2.0 g of PVC and 2.0 g of NaN₃ in 100 mL of DMF. The solvent was allowed to stir at 30 °C for 24 h and precipitated into water/methanol mixture (1/1 by volume), and dried in a vacuum to obtain the PVC-N₃ (Yield:95%). The synthetic route of PVC-N₃ was presented in Fig. 1.

2.4. Preparation of modified PVC (M-PVC)

Modified PVC (M-PVC) was prepared by dissolving 0.64 g of PVC-N₃, 1.02 g (6 mmol) of propargyl ether triethyl citrate, 1 g (6 mmol) of cuprous bromide, 1.82 g (14 mmol) of 5,5-dimethyl-2,2-dipyridyl in 20 mL of DMF, which were introduced in a three-neck flask which was equipped with a mechanical stirrer, nitrogen pipe and thermometer. The mixture was stirred at 30 °C for 24 h. The product was filtered to remove the copper salts, then the mixture was precipitated into water/methanol mixture (1/1 by volume) and dried in a vacuum to obtain the M-PVC (Yield:92%). The preparation of M-PVC was presented in Fig. 1.

2.5. Preparation of pure PVC blend and PVC-DOP blend (D-PVC)

PVC blend was prepared by dissolving 20 g of PVC and 8 g of DOP in 100 mL of THF. The mixture was thoroughly agitated using a mechanical agitator at 160 rpm for 1 h at 60 °C until the mixture presented clear and transparent. The samples were then cast into Petri dishes (diameter 12 cm) and dried at ambient temperature for 7 days to remove traces of residual solvent and to obtain thin films.

2.6. Characterization and measurements

Fourier transform infrared (FT-IR) spectra of PVC, PVC-N₃ and M-PVC were investigated on a Nicolet iS10 FTIR measurement (Nicolet Instrument Corp., USA). The spectra were acquired in the range of 4000 cm⁻¹ to 500 cm⁻¹ at a resolution of 4 cm⁻¹.

¹H NMR measurements were conducted on an AV-400 NMR spectrometer (Bruker Instrument Corp., Germany) at a frequency of 400 MHz CDCl₃ was used as solvent and tetrametylsilane (TMS) as an internal standard.

Elemental analysis was conducted on an elemental PE-2400 analyzer (PERKINELMER Instrument Corp., USA).

Molecular weight of PVC and M-PVC was measured by using an Efficient gel chromatograph made by Waters, USA at 30 °C (flow rate: 1 mL/min, column: mixed PL gel 300 × 718 mm, 25 μm) using THF as solvent.

Thermogravimetric analysis (TGA) was carried out using a TG209F1 TGA thermal analysis instruments (Netzsch Instrument Corp., Germany) in N₂ atmosphere (50 mL/min) at a heating rate of 10 °C/min. 5 mg of samples were put into platinum pans and scanned from 40 °C to 600 °C.

Glass transition temperature (T_g) was characterized using a NETZSCH DSC 200 PC analyzer, the temperature ranged from -60 °C to 120 °C at a heating rate of 20 °C/min [13].

Migration stability of plasticizer was tested in according to ASTM D1239-98. The test temperature was 23 ± 2 °C. The relative humidity was 50 ± 5%. PVC materials were immersed in four different solvents (distill water, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether). PVC materials were settled in 200 mL of four solvent after weighting. The solvent extracted PVC products were rinsed with isoctane and then wiped up using vegetable parchment 24 h later [31–34]. After drying at 30 °C for 24 h and reweighed. The extraction loss was calculated according to Equation (1). Equation (1): Degree of migration = [(W₁-W₂)/W₁] × 100,

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