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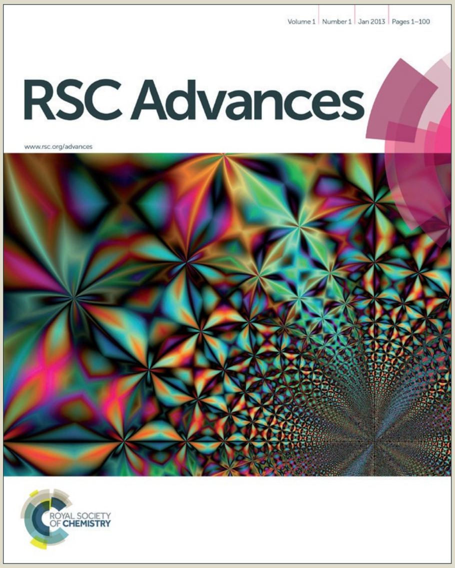

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# Novel Environmentally Sustainable Cardanol-based Plasticizer Covalently Bound to PVC *via* Click Chemistry: Synthesis and Properties

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An approach covalently linked cardanol, a well-known renewable organic resource of the cashew industry, to PVC chains using Click reaction has been studied. Under the conditions, cardanol was covalently linked to PVC chains as natural internal plasticizer. The modified PVC exhibited decreased glass transition temperature, excellent thermal stability and near-zero migration. We believe this approach may help researchers design and explore novel environmentally sustainable plasticizers and apply them in harsh conditions.

## Introduction

Poly(vinyl chloride) (PVC), one of the most pop plastics, can be divided into two types, flexible (plasticized) PVC and rigid PVC (also known as unplasticized PVC, PVC-U). It has been widely used in many areas like artificial leather, medical field, packaging material, toys, bathroom curtains, kitchen floors, pipes and window profiles, due to its high versatility and excellent desirable properties at low cost. However, the application of PVC is limited by its poor processability and inflexibility.[1] In order to obtain the desired flexibility and durability, large amounts of plasticizers are always used by mixing with PVC. Most of them are based on esters of phthalic acid or adipic acid, like Di(2-ethylhexyl) phthalate (DOP) which is by far the most commonly used PVC plasticizer.[2] Due to thermodynamic reasons, however, these plasticizers migrate to the surface of PVC causing progressive loss of its initial properties and serious health hazards.[3-9] For instance, DOP, dibutyl phthalate (DBP) and butyl benzyl phthalate (BBP) have been identified as being toxic for reproduction, and have been restricted in the European Union for use in children's toys since 1999. The research for desirable plasticizers for PVC is therefore receiving a great deal of attention, especially for biomedical applications.

Three approaches have been considered for design of desirable plasticizers: (1) replacing the classical plasticizers by materials that are biocompatible or oligomeric character and, (2) reducing plasticizer leaching and migration from flexible PVC to environments and (3) covalent linkage of plasticizers to PVC chains. As for the first approach, many plasticizers, for instance, epoxidized fatty acid esters, epoxidized vegetable oils plasticizers, phenol alkyl sulfonate plasticizers and polyesters plasticizers have been explored,[10-14] but, the migration of the plasticizers still can not be avoided. For this reason, an approach by reducing plasticizer migration from flexible PVC to the environments has been developed. Some strategies like surface crosslinking, modification of surface hydrophilicity/lipophilicity and surface coating are investigated.[15-21] This approach is to modify the article surface and leaving the plasticizers behind the surface, but the migration of the plasticizers is still not completely avoided since the thermodynamic reasons still remain. Therefore, the approach by incorporating plasticizers into PVC chains through reactions is desirable. For example, DOP can be linked into PVC chain as an internal plasticizer with good plasticizer effect and zero migration *via* the nucleophilic substitution reactions.[22] However, the hazardous DOP still exists and will still cause pollution especially after discarding.[23] For these reasons, if biocompatible plasticizers such as natural products can be incorporated into PVC chains, the approach will be desirable because it can overcome both migration and environmental problem.

Cardanol, a well-known renewable organic resource, deriving from the thermal decomposition of the natural anacardic acids, is the extracted oil from the cashew nutshell and has been used as surface coatings, adhesives, varnishes and paints. It is a mixture compound due to the composition of the long side chain R varies in its degree of unsaturation as scheme 1 shown.[24]

**Scheme 1** Chemical structures of Cardanol.

If cardanol is covalently bound to PVC chains as a part of polymer, it will increase the flexibility of PVC as an environmentally sustainable plasticizer since the long side chain can increase the segmental mobility. However, the question remain unsolved, namely, how to covalently bound cardanol to PVC chains?

PVC can be chemically modified through nucleophilic substitution of its chlorine atoms by some functional groups like thiol and azide.[22,25-30] Considering highly reactive azide can react with alkyne so called Click reaction,[31-34] this current study hence attempts to bound cardanol to PVC chains *via* Click chemistry. In this work, propargyl ether cardanol and azide functional polyvinyl chloride were synthesized firstly and then bound together through Click reaction. The long side chain of cardanol can increase segmental mobility to give the PVC many excellent properties such as the decreased glassy transition temperature ($T_g$), moreover, no cardanol will migrate to the surface of an article. According to the results, we find that cardanol modified PVC has low $T_g$, certain flexibility and near-zero migration, interestingly, while the thermal stability improves.

## Experimental

### Materials

Polyvinyl Chloride (PVC), potass carbonate, dioctyl phthalate (DOP), *N*,*N*-dimethylformamide (DMF), butanone and methanol were purchased from ChengDu Kelong Chemical Reagents Corp. (China). Propargyl bromide, sodium azide ($NaN_3$), copper(I)bromide (CuBr) and 2,2'-dipyridyl were obtained from Gracia Chemical Technology Co. Ltd Chengdu (China). Cardanol was kindly supplied by HDSG Beijing Technology Co. Ltd (China).

### Synthesis of propargyl ether cardanol (CPE)

Cardanol (15 g, 50 mmol), propargyl bromide (6.54 g, 55 mmol), potass carbonate (7.6 g, 55 mmol) and acetone (30 mL) were introduced into a 100 mL three-neck flask. The mixture was stirred at reflux temperature for 12 h. After cooling to room temperature, the mixture was washed by deionized water with 3 times, and the solution was evaporated under vacuum to afford 16 g orange red transparent solution (Yield: 95%).

$^1$H NMR (DMSO-$d_6$, ppm): 2.60 (-C≡C***H***), 4.75 (Ar-C$\boldsymbol{H_2}$-C≡C); FTIR (KBr, cm$^{-1}$): 2123 (-C≡C-) and 3308 (≡C-H).

### Synthesis of azide functional polyvinyl chloride (PVC-$N_3$)

In a 250 mL three-neck flask, PVC (2 g) was dissolved in *N*,*N*-dimethylformamide (DMF) (100 mL), and then sodium azide (2 g) was added. The solution was stirred at room temperature for 24 h and precipitated into methanol/water mixture (2/1 by volume).

$^1$H NMR (DMSO-$d_6$, ppm): 4.59 ($N_3$-C***H***-$(CH_2)_2$ and Cl-C***H***-$(CH_2)_2$), 2.14 and 2.38 ($N_3$-CH-$(C\boldsymbol{H_2})_2$ and Cl-CH-$(C\boldsymbol{H_2})_2$); FTIR (KBr, cm$^{-1}$): 2114 (-$N_3$). Found C 39.37%, H 5.33%, N 3.32%, and Cl 51.98%. Approximately 10% of chlorine units were replaced by -$N_3$.

### Synthesis of polyvinyl chloride with propargyl ether cardanol side groups (PVC-CPE)

PVC-$N_3$ (0.64 g), propargyl ether cardanol (1.02 g, 3 mmol), copper(I)bromide (1 g, 6 mmol), 2,2'-dipyridyl (1.8 g, 14 mmol) and dry DMF (20 mL) were introduced into a three-neck flask under a dry nitrogen atmosphere. The mixture was stirred at ambient temperature for 24 h. Finally, the mixture, which was filtered to remove copper salts, was poured into methanol (200 mL) and the precipitate was filtered and dried in a vacuum oven to obtain the modified polymer (denoted PVC-CPE).

$^1$H NMR (DMSO-$d_6$, ppm): 1.3 (-C$\boldsymbol{H_2}$), 2.14 and 2.38 (triazole -CH-$(C\boldsymbol{H_2})_2$ and Cl-CH-$(C\boldsymbol{H_2})_2$), 4.52 (triazole-C***H***-$(CH_2)_2$ and Cl-C***H***-$(CH_2)_2$), 4.9 (triazole-C$\boldsymbol{H_2}$-O-Ar), 5.0-6.0 (C=C***H***-), 6.9-7.2 (Aromatic ***H***), 7.25 (N-C***H***=C- of triazole); FTIR (KBr, cm$^{-1}$): 1042 and 1152 (Ar-O-C), 1486, 1586, 1602 and 3009 (Aromatic).

### Preparation of the blend of polyvinyl chloride and dioctyl phthalate (PVC-DOP)

For comparison, the blend with a glassy transition temperature similar to PVC-CPE was prepared as follows: PVC (9.2 g), DOP (0.8 g) and butanone (30 mL) were introduced into a 50 mL flask. The mixture was stirred at 65 °C until PVC and DOP mixed completely. After removing the solvent, we obtained a transparent product named as PVC-DOP.

### Characterizations and Measurements

Fourier transform infrared (FTIR) studies were performed in KBr pellets using a Nicolet iS10 FTIR spectrometer at a resolution of 4 cm$^{-1}$. The scanned wavenumbers range from 4000 to 400 cm$^{-1}$.

$^1$H NMR measurements was conducted on a Bruker TD-65536 NMR (400 MHz) in $CDCl_3$ or DMSO-$d_6$ as solvent with tetramethylsilane (TMS) as the internal reference.

Elemental analysis was conducted with Elementar vario EL III analyzer.

Calorimetric measurements of the modified PVC samples were carried out using a NETZSCH DSC 200 PC analyzer, which was purged with nitrogen gas and quenched with liquid nitrogen. Samples (about 10 mg) were heated up to 150 °C and quenched. The $T_g$ values reported were taken from the second runs and correspond to the midpoint of the DSC curves measured from the extension of the pre- and posttransition baseline.

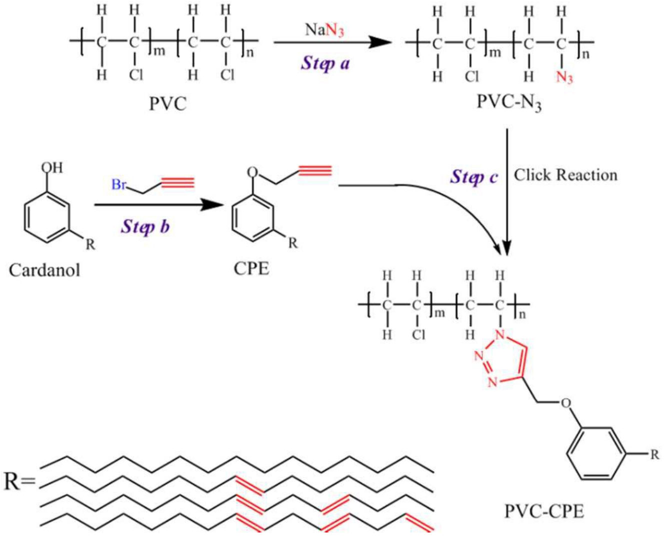
Migrations of plasticizers were evaluated using ultraviolet spectroscopy. PVC-DOP or PVC-CPE (0.5 g) was immersed in *n*-heptane (25 mL) at 40 °C. After soaking for respectively 30, 150, 270, 390, 510, 630, 1230, 1470 and 3210 minutes, transfer 0.5 mL of the solution to a conical flask and dilute with 5.0 mL of *n*-heptane. Then, the migrations can be evaluated through detecting these dilute solutions using a Shimadzu UV-2501PC spectrophotometer (Japan). For PVC-CPE, the UV spectra of the dilute solutions (Fig. S1 in Supporting Information) were recorded at ambient temperature from

220 to 500 nm. In the case of PVC-DOP, the concentrations of DOP in the diluted solutions can be measured *via* probing the absorbances using the UV spectroscopy at 273 nm assigned to the aromatic structure of DOP.[35] Finally, the migrated DOP's concentrations can be obtained from the Absorbance-Concentration standard curve (Fig. S2 in Supporting Information), and the 11 times concentrations of the dilute solutions were approximately the amount of the migrated DOP.

TGA was performed with a NETZSCH TA Instruments' High Resolution TG 209F1 thermogravimetric analyzer under nitrogen atmosphere from 40 to 700 °C at a heating rate of 10 °C/min.

## Results and discussion

This work aims to covalently bind environmentally sustainable cardanol to PVC chains as an internal plasticizer through Click reaction, propargyl ether cardanol (Scheme 2, *Step b*) and azide functional polyvinyl chloride (Scheme 2, *Step a*) were thus synthesized. The chemical structure of propargyl ether cardanol (CPE) was confirmed by FTIR and $^1$H NMR. In the FTIR spectrum of CPE (Fig. 1, CPE), the absorptions at 2123cm$^{-1}$ and 3308 cm$^{-1}$ which respectively corresponded to -C≡C- and ≡C-H were observed, suggesting that produced the Click functionality in CPE. The $^1$H NMR spectrum of CPE and the assignment were shown in Fig. 2 (1). The signals at 2.60 and 4.75 ppm were respectively assigned to -C≡C***H*** and Ar-C***H*$_2$**-C≡C which further confirmed the production of -C≡C***H*** structure.



**Scheme 2** Synthesis of PVC-CPE.

For the synthesis of azide functional polyvinyl chloride (PVC-N$_3$), the chlorine atoms of PVC have been chemically modified by sodium azide (NaN$_3$) *via* nucleophilic substitution. Approximately 10% of chlorine units were replaced by azides (Scheme 2, *Step a*) as detecting by elemental analysis. Fig. 2 (2) showed the $^1$H NMR spectrum of PVC-N$_3$. The signals of N$_3$-C***H***-(CH$_2$)$_2$ and Cl-C***H***-(CH$_2$)$_2$ appeared at 4.59 ppm, whereas the N$_3$-CH-(C***H*$_2$**)$_2$ and Cl-CH-(C***H*$_2$**)$_2$ resonance appeared at 2.14 and 2.38 ppm. The PVC-N$_3$ was also supported by the observation of the azides stretching band at 2114 cm$^{-1}$ in the FTIR spectrum of PVC-N$_3$ shown in Fig. 1.

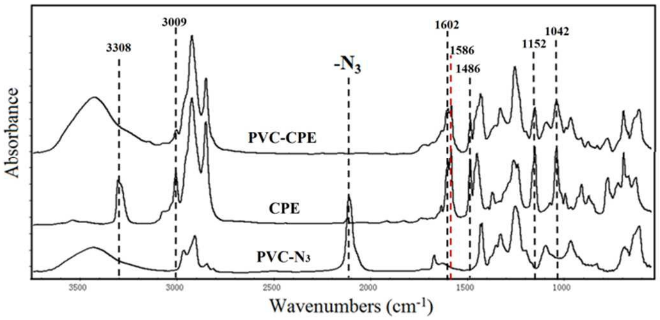


**Fig. 1** FTIR spectra of PVC-N$_3$, CPE and PVC-CPE.

In this work, the Click reaction has been explored. PVC-N$_3$ was dissolved in DMF and reacted with CPE in the presence of CuBr/bipyridine ligand at room temperature (Scheme 2, *Step c*). After removing the catalyst, the modified PVC (PVC-CPE) was precipitated and dried. FTIR was used to understand the reaction between PVC-N$_3$ and CPE, and the reaction were recorded and shown in Fig. 1. The -N$_3$ of PVC-N$_3$ band at 2114 cm$^{-1}$, and the -C≡CH of CPE at 2123 and 3308 cm$^{-1}$ completely disappeared after the Click reaction, indicating complete reaction of the -N$_3$ band. Moreover, the absorption appeared at 1042, 1152, 1486, 1586, 1602 and 3009 cm$^{-1}$ which corresponded to the CPE were observed in PVC-CPE, demonstrating CPE was anchored into PVC. The $^1$H NMR spectrum was applied to further study the Click reaction, Fig. 2 (3). The characteristic resonances of N-C***H***=C- of triazole appeared at 7.25 ppm, suggesting that -N$_3$ generated into triazole *via* Click reaction. The signals at 2.14, 4.52 and 4.9 ppm were respectively assigned to triazole-CH-(C***H***$_2$)$_2$, triazole-C***H***-(CH$_2$)$_2$ and triazole-C***H***$_2$-O-Ar, further confirming the Click reaction between PVC-N$_3$ and CPE. Moreover, the presence of signals at 1.3, 5.0-6.0 and 6.9-7.2 ppm for cardanol indicated cardanol was incorporated into PVC chain through Click reaction. This will increase the PVC chains' mobility which led to decrease of the glass transition temperature.

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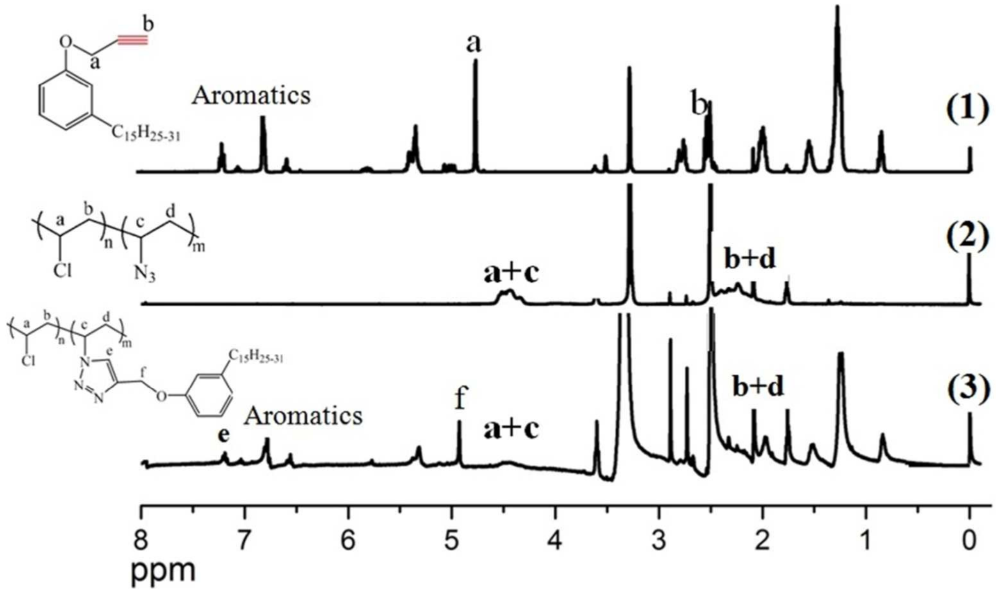

**Fig. 2** $^1$H NMR (DMSO-$d_6$) spectra of (1) CPE, (2) PVC-$N_3$, and (3) PVC-CPE.

### Glass Transition Temperature

To probe the plasticizer efficiency of the novel additives, the glass transition temperatures ($T_g$s) of PVC, PVC-$N_3$, PVC-DOP and PVC-CPE are hence measured using DSC, and the measurements are plotted in Fig. 3.

Compared to PVC, as can be seen, a slight decrease of $T_g$ was observed in PVC-$N_3$, are probably attributed to the destroy of macromolecular chain regularity. This further illustrates that the chlorine atoms of PVC have been partly replaced by azides during the reaction between PVC and sodium azide. For PVC-CPE, the measured value of PVC-CPE was 51.0 °C and close to that of the blend of PVC and DOP (48.8 °C, when the content of DOP is 8 wt%). A decrease of about 36 °C was detected, indicating covalently bond cardanol to PVC chains *via* Click reaction can decrease the $T_g$ efficiently. This is probably because the long side chain can increase the distance between the PVC chains and decrease the intermolecular forces which helps to increase the segmental mobility leading to the decrease $T_g$.

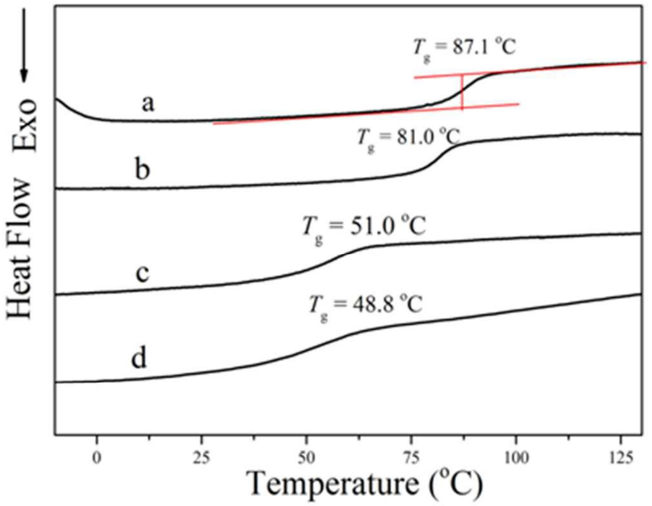

**Fig. 3** The DSC curves of PVC (a), PVC-$N_3$ (b), PVC-CPE (c) and PVC-DOP (d).

### Migration of Plasticizers

To understand migration tendency of the plasticizers, the migration behavior of the modified PVC was tested by extraction experiments using *n*-heptane at 40 °C. The amount of the migrated plasticizers was quantified by ultraviolet spectroscopy, and extractions of plasticized PVC are presented in Fig. 4.

Because the physical interaction force between DOP and PVC can not avoid the migration, as can be seen from Fig. 4, PVC-DOP loses the most amount of additive after less than 10 hours. In contrast, no noteworthy loss of plasticizer in the ultraviolet spectroscopy (Fig. S1 in Supporting Information) is observed in PVC-CPE, since cardanol is covalently linked to the PVC chain *via* Click reaction. This illustrates that the migration of natural plasticizer can be nearly avoided using Click reaction.

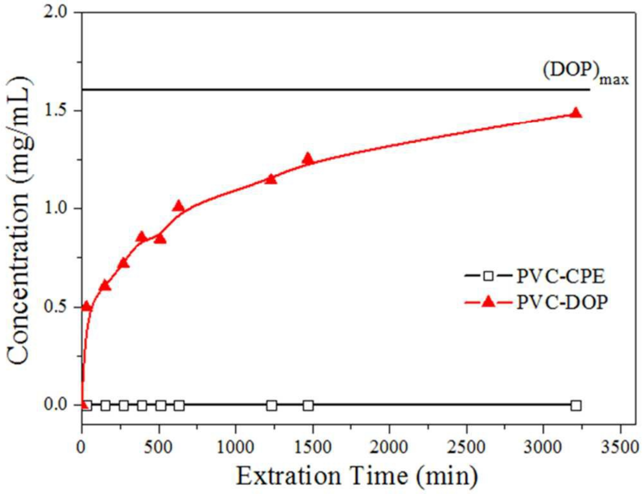

**Fig. 4** Extraction of plasticized PVC with heptane at 40 °C: PVC-DOP (▲) and PVC-CPE (□).

**Thermal stability**

As low molecular weight compounds, plasticizers volatilize easily from the articles to environment to harm the applications and public health particularly at evaluated temperature.[36,37] The thermal stability of PVC-CPE and PVC-DOP are therefore analyzed by TGA. The TGA thermograms are shown in Fig. 5. As can be seen, PVC-DOP exhibited poor thermal stability, probably caused by the volatilization of DOP at high temperature. The 1%, 5% and 50% weight loss temperatures of PVC-DOP were 107 °C, 160 °C and 296 °C, respectively. These values for PVC-CPE were respectively 143 °C, 225 °C and 387 °C, suggesting that PVC-CPE had excellent thermal stability. This probably attributed to the triazole derived from the Click reaction between CPE and PVC-$N_3$. The results also indicated that natural plasticizers can be linked to PVC chains and enhance the thermal stability *via* Click reaction. This approach may help the researchers study and apply other natural plasticizers.

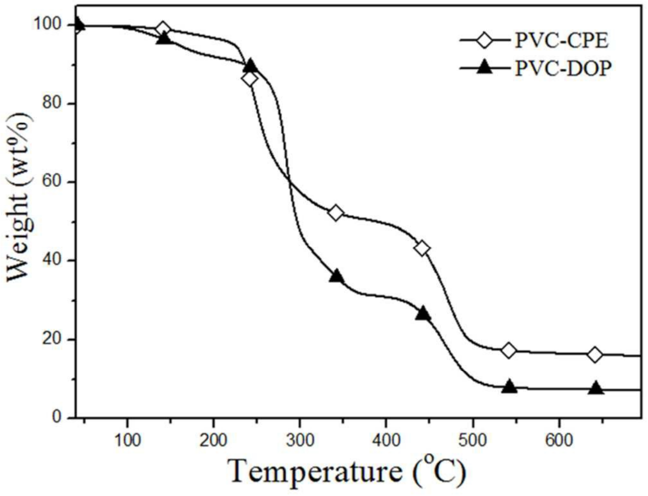

**Fig. 5** The TGA curves of PVC-CPE and PVC-DOP.

## Conclusions

In this work, we have developed an approach, covalently linked natural sustainable plasticizer to PVC using Click reaction, to avoid migration of the additive. The synthesis and the modified PVC were studied in detail. Under the selected experimental conditions, cardanol is covalently linked to PVC chains as natural internal plasticizer using Click reaction. The glass transition temperature of modified PVC is largely reduced and close to that of the blend of PVC and DOP (when the content of DOP is 8 wt%), which reveals that sustainable cardanol is a good candidate for plasticizer. More interestingly, the plasticizer modified PVC exhibits near-zero migration in *n*-heptane at 40 °C, showing obvious internal plasticizing effect. Another interesting result is that the modified PVC presents excellent thermal stability may help this approach to application at elevated temperature. We believe that the plasticizers can satisfy the demands of plasticization and, can help researchers design and explore novel environmentally sustainable plasticizers and apply them in harsh conditions.

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## Notes and references

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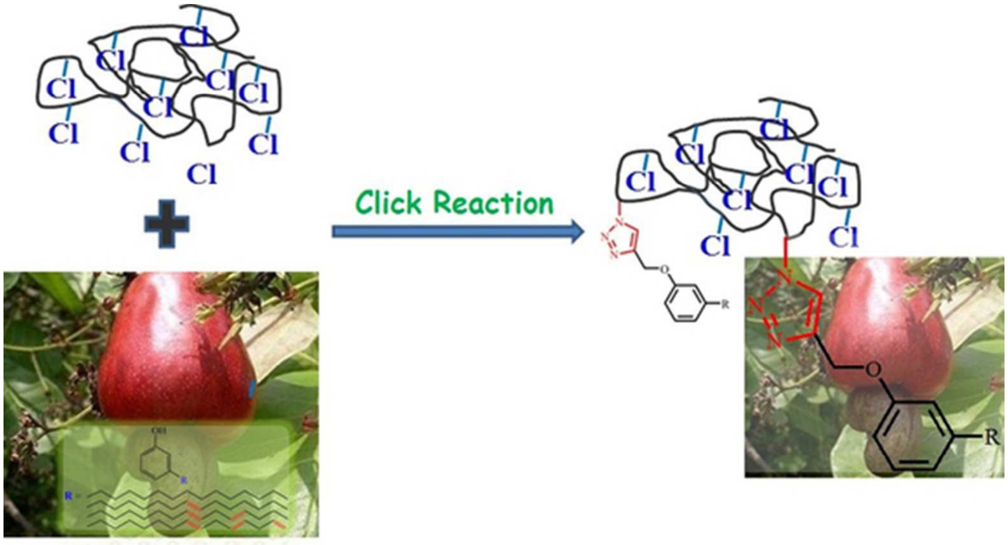

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