

A strategy to prepare internally plasticized PVC using a castor oil based derivative

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Abstract—Internally plasticized PVC was prepared via chemical reaction of azide PVC and alkynyl group containing castor oil methyl ester. The chemical structure of alkynyl group containing castor oil methyl ester and internally plasticized PVC was characterized with FT-IR and ¹H NMR. Properties of internally plasticized PVC, including thermal stability, tensile tests and resistance to extraction in different solvents, was investigated. The results showed that alkynyl group containing castor oil methyl ester, as internal plasticizer of PVC, not only decreased the T_g of PVC from 84.6 °C to 41.6 °C efficiently, but also presented no plasticizer loss in five different solvents. The tensile tests showed that elongation at break and tensile strength of internally plasticized PVC was 353.8% and 18.1 MPa. The internally plasticized PVC has potential application in replacing the traditional PVC material in PVC products with high durability.

Keywords: Polyvinyl Chloride, Castor Oil, Plasticizer, Internal Plasticizing Method

INTRODUCTION

Polyvinyl chloride (PVC) has been widely used to produce toys, wire and cable, food packing and leathers [1-3]. But PVC is too stiff to be processed and usually blends with a large amount of plasticizers to improve its flexibility and processability [4]. Phthalic plasticizers, as the main plasticizer, account 80% of the plasticizer consumption around the world [5,6]. Though the plasticizing efficiency of phthalic plasticizers is higher and its price is low, their use has been restricted in food packing materials and children's toys due to their potentially toxic effect on the human body [7-10]. Therefore, researchers have paid attention to plasticizers derived from renewable resources [11]. Cardanol based plasticizer [12], chlorinated phosphate ester based on castor oil [13], epoxidized jatropa oil [14], epoxidized linseed oil [15], palm oil based polyester plasticizer [16], and epoxidized soybean oil (ESO) [17] have been synthesized and investigated. But these plasticizers are external plasticizers, which are used to improve the plasticizing properties of PVC products by blending method. The blending method cannot stop plasticizers migrating from PVC products with the increase of time. The internal plasticizing strategy can solve the problem. Jia group [18-21] did excellent work on internally plasticized strategy. Cardanol, tung oil, castor oil and waste cooking oil methyl ester based internal plasticizer improved the flexibility of PVC materials, but also there was no plasticizer migration. They provided several methods to improve the solvent resistance and flexibility of PVC materials using biomass resources and provided a new direction for the chemical utilization of biomass resources. In addition, Navarro group [22] and Lee group [23] also reported that internally plasticized methods were used to prepared flexible PVC materials without migration.

In this work, we provided a method to synthesis no migration PVC materials using castor oil derivative as internal plasticizer. First, alkynyl group containing castor oil based derivative was synthesized. Secondly, azide PVC material was synthesized from PVC and sodium azide. The plasticized PVC materials without migration were prepared from alkynyl group containing castor oil based derivative and azide PVC material via click chemistry. Chemical structure of the obtained plasticized PVC materials was characterized. Thermal stability, resistance to extraction in different solvents and mechanical properties of the PVC films was investigated.

EXPERIMENTAL DETAILS

1. Materials and Chemicals

Castor oil, caustic potash (KOH), sulfuric acid, propargyl bromide solution, potassium carbonate, sodium azide, *N,N*-dimethylformamide (DMF), anhydrous methanol, acetone, methanol, acetic acid, petroleum ether, 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 Rong Bei Chemical Technology Co., Ltd. (Shanghai, P. R. China), K-value of 60.5; average M_w~42,000, average M_n~25,000.

2. Methods

2-1. Synthesis of Castor Oil Methyl Ester

Castor oil (100 g), anhydrous methanol (20 g) and KOH (0.90 g) were mixed in a 500 mL round bottom flask. The mixture was stirred at 45 °C for 6 h. Castor oil methyl ester was obtained after washing with sulfuric acid solution and water, and removing water with a rotary evaporator [21].

2-2. Synthesis of Alkynyl Group Containing Castor Oil Methyl Ester

Castor oil methyl ester (50 mmol), propargyl bromide solution (55 mmol), potassium carbonate (55 mmol) were dissolved in 30 mL of acetone. The mixture was stirred at 65 °C for 12 h. The mixture was washed with deionized water three times. The product

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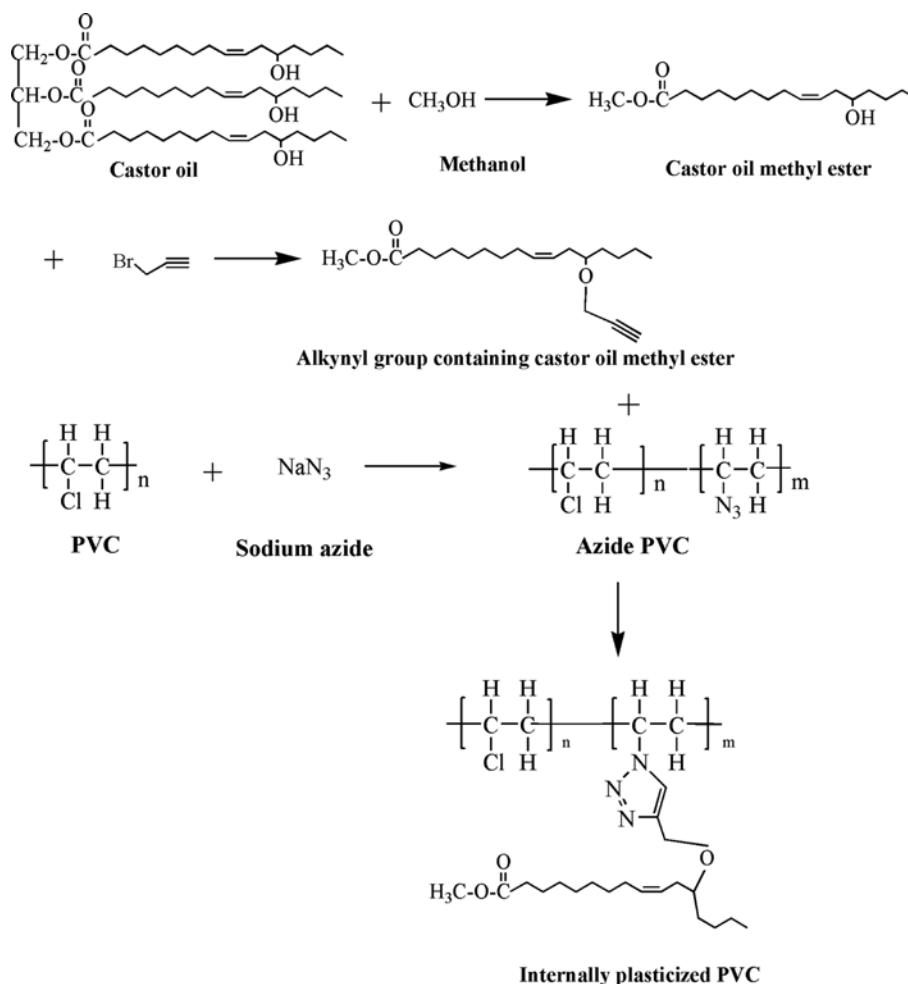


Fig. 1. Synthesis of internally plasticized PVC.

was obtained after evaporating under vacuum. The preparation of alkynyl group containing castor oil methyl ester is presented in Fig. 1.

2-3. Synthesis of Azide PVC

Two grams of PVC and the same quality of NaN_3 were mixed in 100 mL of DMF. The mixture was stirred at 30°C for 24 h to finish the reaction. Then azide PVC was obtained after precipitating into water/methanol mixture (1/1 by volume) and drying in a vacuum to obtain the azide PVC [20].

2-4. Synthesis of Internally Plasticized PVC

Azide PVC (2 g), alkynyl group containing castor oil methyl ester (1.0 g), cuprous bromide (0.52 g), 5,5-dimethyl-2,2-dipyridyl (1.30 g) were dissolved in 20 mL of DMF, which was stirred at room temperature for one day in N_2 atmosphere. The mixture was precipitated into water/methanol mixture (1/1 by volume) and dried in a vacuum to obtain the internally plasticized PVC. The preparation of internally plasticized PVC is presented in Fig. 1.

2-5. Preparation of PVC Films

Internally plasticized PVC (3 g) was dissolved in 100 mL of THF and stirred for one hour at 60°C , then the mixture was cast into Petri dishes (diameter 12 cm). Internally plasticized PVC film was obtained after drying and removing traces of residual THF. Pure

PVC films and PVC(3 g)/DOP(1.5 g) films were also prepared using the same method. Three grams of PVC and PVC(3 g)/DOP(1.5 g) was, respectively, dissolved in THF and then cast into Petri dishes (diameter 12 cm). The pure PVC films and PVC(3 g)/DOP(1.5 g) films were obtained after removing solvent.

2-6. Measurements

The chemical structures of the castor oil methyl ester, alkynyl group containing castor oil methyl ester and internally plasticized PVC were detected using Fourier transform infrared (FTIR) spectra (Nicolet IS10 instrument, USA, KBr pellet) over a range of $4,000-500\text{ cm}^{-1}$. The ^1H NMR spectra of castor oil methyl ester, alkynyl group containing castor oil methyl ester and internally plasticized PVC were investigated by a Bruker ARX 300 spectrometer (Bruker Co., Germany) at room temperature. Thermogravimetric analysis (TGA) was carried out on a 409PC thermogravimetric analyzer (Netzsch Co., Germany). The internally plasticized PVC films were heated from 40 to 600°C at a rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere. FT-IR spectra of the pyrolysis product during the thermal degradation process were collected. Glass transition temperature (T_g) of internally plasticized PVC was characterized using a NETZSCH DSC 200 PC analyzer; the temperature ranged from -20°C to 100°C at a heating rate of $20^\circ\text{C}/\text{min}$. Tensile strength and elonga-

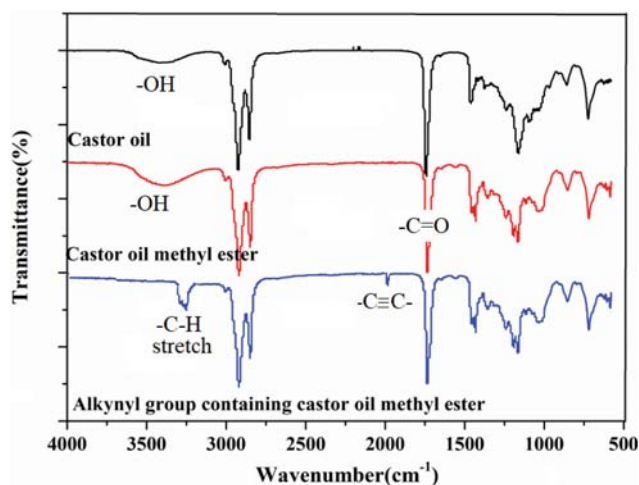


Fig. 2. FT-IR spectrum of castor oil, castor oil methyl ester and alkynyl group containing castor oil methyl ester.

tion at break of the internally plasticized PVC films were measured through a SANS CMT-4303 universal testing machine (Shenzhen Xinsansi Jiliang Instrument Co., China) with cross-head speed of 10 mm/min, according to ISO 527-2: 1993. Leaching tests were carried out according to ASTM D1239-14 and references [24-26]. A certain amount of internally plasticized PVC and PVC films was immersed in five different solvents (distilled water, olive oil, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether) for one day. Then PVC and internally plasticized PVC films were dried and reweighed. The resistance to extraction was calculated according to Eq. (1).

$$\text{Resistance to extraction} = [(W_1 - W_2) / W_1] \times 100 \quad (1)$$

where W_1 = initial weight of test specimen, and W_2 = final weight of test PVC specimens.

RESULTS AND DISCUSSION

1. Chemical Structure of Alkynyl Group Containing Castor Oil

1-1. FT-IR

The FT-IR spectra of castor oil, castor oil methyl ester and alkynyl group containing castor oil methyl ester are presented in Fig. 2. FT-IR spectra of castor oil and castor oil methyl ester are similar; the absorption band at about 3370 cm^{-1} was attributed to -OH groups, which was connected to the fatty acid chains. The absorption at about 3007.70 cm^{-1} corresponded to stretching vibration of C=C derived from castor oil. The absorption at about 2931 cm^{-1} and 2959 cm^{-1} was attributed the $-\text{CH}_2-$ and $-\text{CH}_3$ groups [27-29]. FT-IR of alkynyl group containing castor oil showed different absorption band compared with castor oil and castor oil methyl ester. The absorption band at about 3370 cm^{-1} disappeared. New peak at 3270 cm^{-1} was attributed to alkyne C-H stretch, and the C=C stretch characteristic absorption peak appeared at 2100 cm^{-1} [27-29]. All of the results illustrated that castor oil methyl ester and alkynyl group containing castor oil was obtained.

1-2. ^1H -NMR

^1H NMR spectra of castor oil, castor oil methyl ester and alkynyl

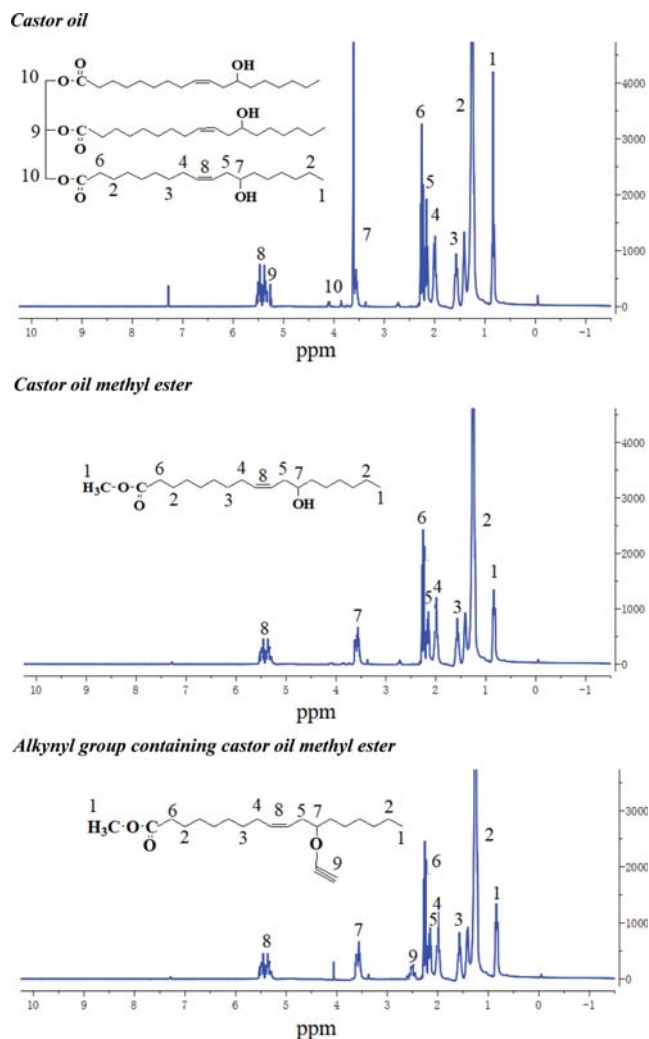


Fig. 3. ^1H NMR of castor oil, castor oil methyl ester and alkynyl group containing castor oil methyl ester.

group containing castor oil were also investigated and compared. Fig. 3 shows the ^1H NMR spectra of castor oil and castor oil methyl ester. They look similar because they have similar chemical structure. Peak 1 at 0.89 ppm was attributed to protons $[-\text{CH}_3]$ of methyl groups. The strong peak 6 at 2.31 ppm corresponded to protons $[-(\text{CH}_2)_n-\text{CO}]$ of fatty acids. Peak 7 at 3.5-3.7 ppm was attributed to methylene protons of glycerol [27-29]. The peak of protons of castor oil methyl ester at 3.5-3.7 ppm became weak compared to castor oil. The peak at 5.3-5.6 ppm is a characteristic peak for protons $[-\text{CH}=\text{CH}-]$ of olefinic hydrogens. The signal at 2.1 ppm corresponded to $-\text{CH}_2-$ of $\text{HO}-\text{C}-\text{CH}_2-\text{C}-$ [27-29]. Fig. 3 shows the ^1H NMR of alkynyl group containing castor oil. The new signal at 4.2 ppm was attributed to protons of $-\text{CH}_2-$ connected to the alkynyl groups [23]. The new peak at around 2.5 ppm was assigned to protons of alkynyl groups. The change of ^1H NMR spectra indicated the alkynyl group containing castor oil was obtained.

2. Chemical Structure of Azide PVC and Internally Plasticized PVC

2-1. FT-IR

Fig. 4 shows the FT-IR spectrum of alkynyl group containing cas-

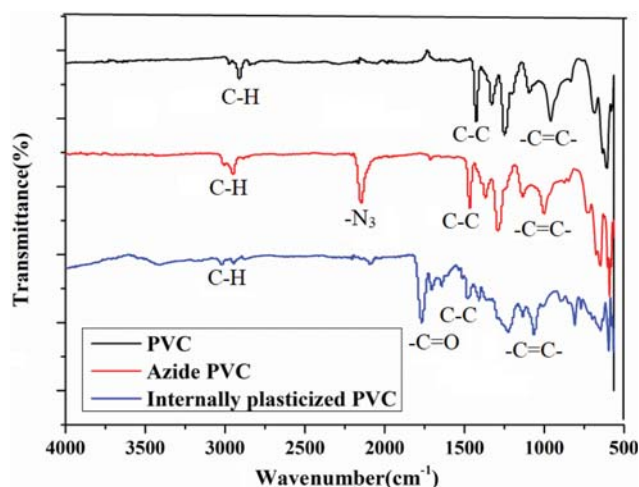


Fig. 4. FT-IR spectrum of PVC, azide PVC and internally plasticized PVC.

tor of PVC, azide PVC and internally plasticized PVC. A new strong peak can be observed at $2,110\text{ cm}^{-1}$ in the FTIR spectrum of azide PVC compared with PVC, which was the characteristic absorption peak of the azide group [30-32]. The results indicated that azide PVC was obtained. The FTIR spectrum of internally plasticized PVC presented the characteristic absorption of C-H stretch, C-C bonds, and the C=C stretching vibration mode at $2,911$, $1,589$ and $1,160\text{--}1,450\text{ cm}^{-1}$ [27-29], which derived from alkynyl group containing castor oil. The results illustrated that internally plasticized PVC was synthesized.

2-2. ^1H -NMR

To further detect the chemical structure of internally plasticized PVC, ^1H NMR of PVC and internally plasticized PVC was investigated and shown in Fig. 5. ^1H NMR spectra of PVC and azide PVC present similar. The signal at $\delta 4.5$ ppm corresponded to protons of $-(\text{CH}_2)-\text{CHCl}$. The signal of protons of $-\text{CHCl}-(\text{CH}_2)-$ appeared at $\delta 2.2$ ppm. However, some new signals appeared at $\delta 5.6$, $\delta 2.75$

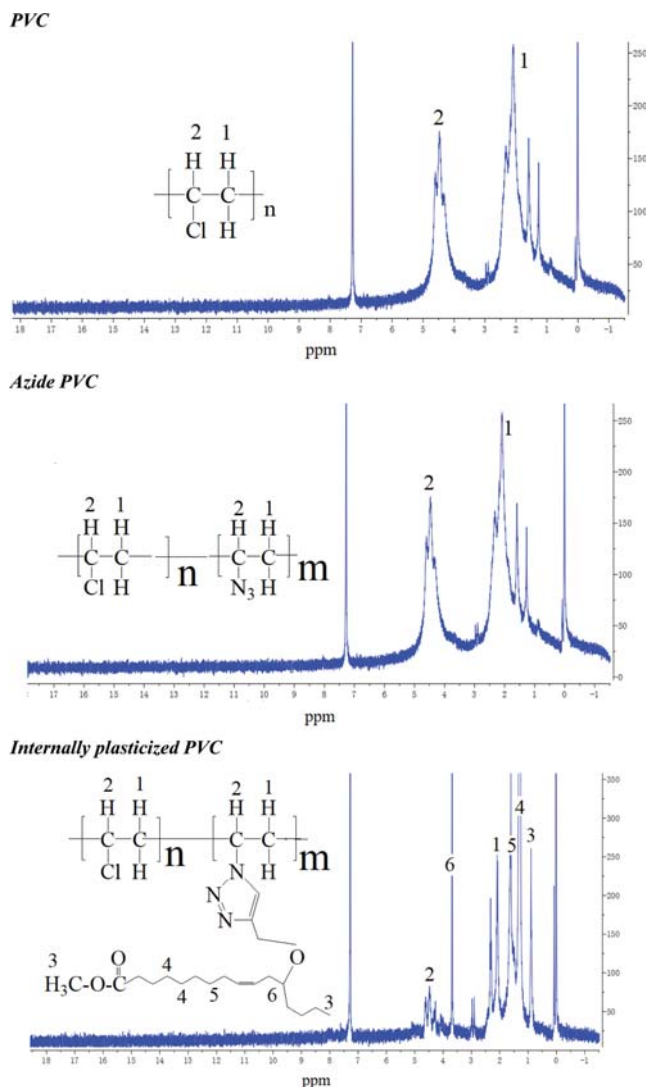
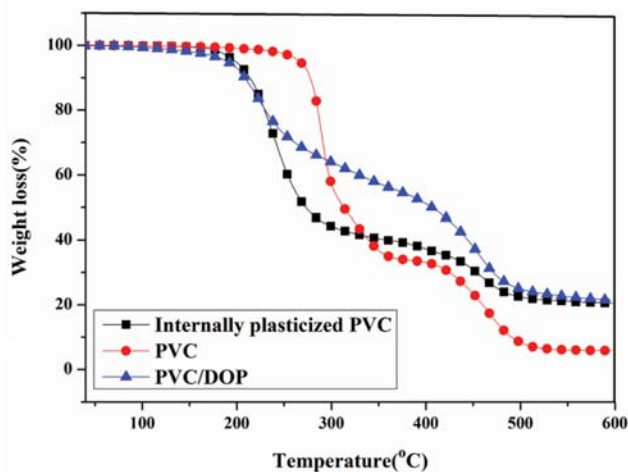


Fig. 5. ^1H NMR spectra of PVC, azide PVC and internally plasticized PVC.

TGA curves



DTG curves

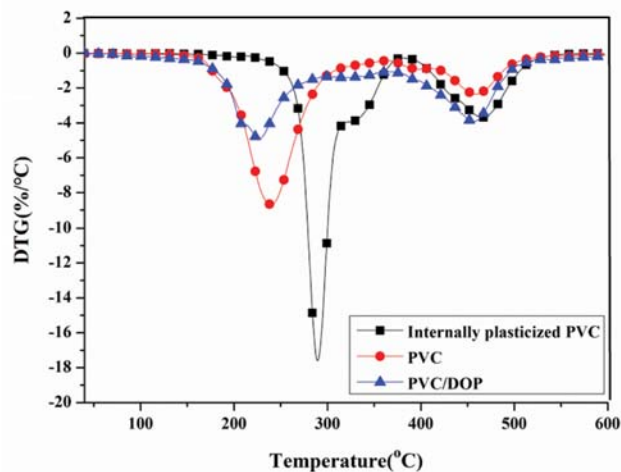


Fig. 6. TGA curves and DTG curves of PVC, PVC/DOP and internally plasticized PVC.

Table 1. Thermal degradation data of PVC and internally plasticized PVC

Samples	$T_d/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$T_g/^\circ\text{C}$	Char residue/%
PVC	276.1	308.0	84.6	9.12
Internally plasticized PVC	223.6	287.0	41.6	21.30
PVC/DOP	216.8	371.4	23.2	22.10

and $\delta 0.90$ ppm in the ^1H NMR of internally plasticized PVC, which were associated with the protons of olefin groups, methylene groups and methyl groups of branched chains derived from alkynyl group containing castor oil [30-32], respectively. The results indicated that alkynyl group containing castor oil had been connected onto the PVC as branched chains.

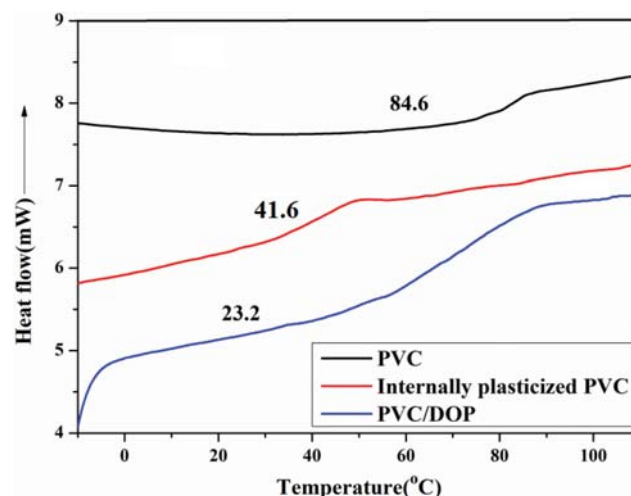
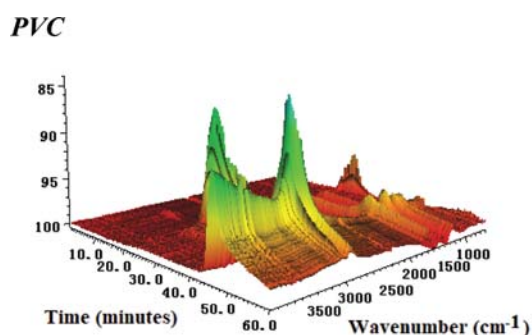
3. Performances of Internally Plasticized PVC

3-1. TGA

Thermal stability of PVC and internally plasticized PVC film was characterized and compared. TGA and DTG results are illustrated in Fig. 6. The thermal data is shown in Table 1. Fig. 6 shows TGA curves of PVC and internally plasticized PVC, HCl was released at around 200°C - 400°C . The DTG curves of PVC, PVC/DOP and internally PVC also showed two pyrolysis processes. Decomposition temperature (T_d), the mass loss of 50% (T_{50}) and char residue are summarized in Table 1. T_d and T_{50} of PVC film was higher than internally plasticized PVC. T_d for PVC, PVC/DOP and internally plasticized was 276.1°C , 216.8°C and 223.6°C , respectively. The results indicated that azide groups and DOP decreased the thermal stability of PVC. In addition, the amount char residue of PVC, PVC/DOP and internally plasticized PVC was 9.12%, 21.30% and 22.10%, which illustrated that the internal plasticizing method and the addition of DOP increased char residue of PVC material. Thermal stability of the obtained internally plasticized PVC is similar to PVC grafted with phosphorus containing castor oil based derivatives [21], because active azido groups existed in the chemical structure of both of the two kinds of internally plasticized PVC materials.

3-2. TGA-FTIR

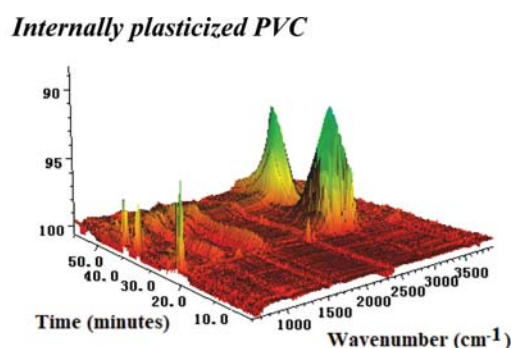
The pyrolytic composition of PVC and internally plasticized PVC was detected using the TGA-FTIR technology. The results are in Fig. 7. As seen from the TGA-FTIR spectrum of PVC, at the temperature of fastest decomposition of 300°C , CO_2 ($2,372\text{ cm}^{-1}$), CO

**Fig. 8. DSC curves of PVC, PVC/DOP and internally plasticized PVC.**

($2,150\text{ cm}^{-1}$), THF ($2,968\text{ cm}^{-1}$), C_6H_6 ($3,086$ and $1,585\text{ cm}^{-1}$) and HCl ($2,885.9\text{ cm}^{-1}$) were released for PVC [29,33-36], while some esters ($1,743$, $1,267$, and $1,103\text{ cm}^{-1}$) and azide groups ($2,150\text{ cm}^{-1}$) were detected in the TGA-FTIR spectrum of internally plasticized PVC. The azide groups were produced from pyrolysis of internally plasticized PVC, which made internally plasticized PVC less stable due to the instability of azide groups.

3-3. DSC

Compatibility and plasticizing efficiency of the internal plasticizing method was evaluated by DSC. The T_g of PVC and internally plasticized PVC was measured by DSC. Fig. 8 presents the DSC curves of PVC, PVC/DOP and internally plasticized PVC, and the glass transition temperature (T_g) values are shown in Table 1. T_g for PVC, PVC/DOP and internally plasticized PVC is 41.6°C , 23.2°C and 84.6°C , respectively. The results show both the internally plasticized method and DOP can decrease the T_g of PVC materials. T_g of the obtained internally is similar to the internally plasticized PVC materials via covalent attachment of aminated tung oil methyl ester [18] and nonmigrating plasticized PVC modified with mannich base of waste cooking oil methyl ester [19], because all of the three kinds of internally plasticized are grafted with long fatty hydrocarbon chain. But the plasticizing efficiency of internally plasticized method was lower than DOP.

**Fig. 7. TGA-FTIR of PVC and internally plasticized PVC.**

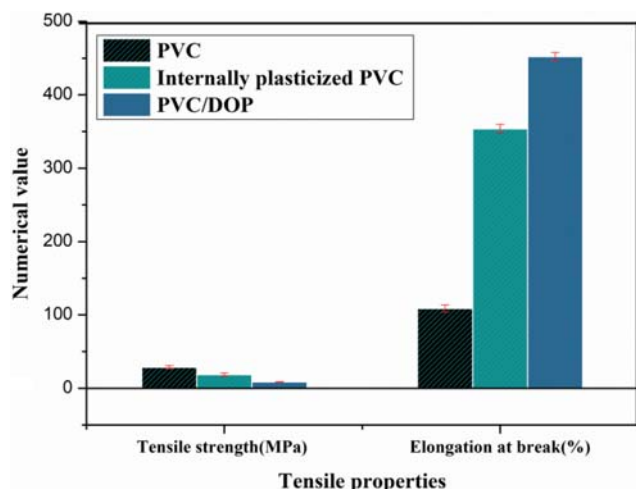


Fig. 9. Tensile strength and elongation at break of PVC, PVC/DOP and internally plasticized PVC.

3-4. Tensile Tests

The elongation at break and tensile strength of PVC film, PVC/DOP and internally plasticized PVC are presented in Fig. 9. PVC/DOP shows the highest elongation at break of 438.2% and the lowest tensile strength of 12.6 MPa among the three kinds of PVC materials, which indicates that the plasticizing efficiency of DOP was better than internally plasticized method. However, internally plasticized PVC shows higher elongation at break of 353.8% and low tensile strength of 18.1 MPa than PVC. The elongation at break and tensile strength of PVC was 108.4% and 28.6 MPa. The results indicate that the covalent connection of alkynyl group containing castor oil methyl ester had a plasticizing effect on PVC.

3-5. Leaching Tests

The resistance to extraction of internally plasticized PVC and PVC plasticized the commercial plasticizer DOP was investigated and compared by the leaching tests using five different solvents and the results are presented in Fig. 10. Every value was the average of the values for five specimens of the same composition. As

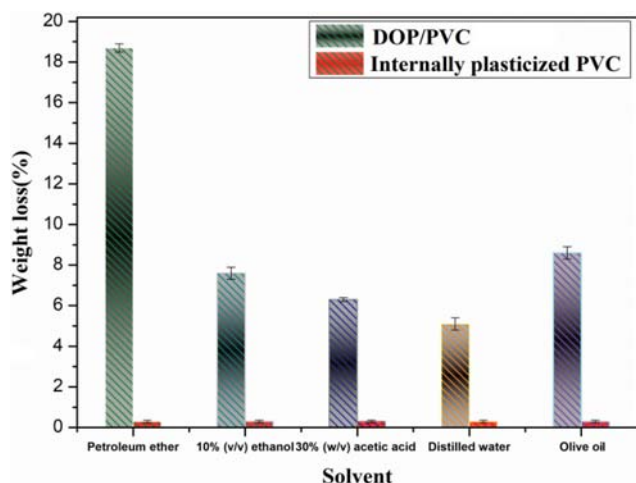


Fig. 10. Resistance to extraction results of internally plasticized PVC and DOP/PVC.

seen from Fig. 10, the loss of the internally plasticized PVC was zero in these five different solvents. But the weight loss of DOP/PVC was 18.7, 7.6, 6.3, 5.1 and 8.6% in petroleum ether, 10% (v/v) ethanol, 30% (w/v) acetic acid, distilled water and olive oil, respectively. It is indicated that the internal plasticizing strategy can avoid the loss of plasticizer.

CONCLUSIONS

Castor oil was modified and used as internal plasticizer for preparing internally plasticized PVC. The results showed that castor oil based internal plasticizer not only decreased the T_g of PVC from 84.6 °C to 41.6 °C efficiently, but also presented no plasticizer loss in five different solvents. The tensile tests showed that internally plasticized PVC presented high elongation at break of 353.8% and low tensile strength of 18.1 compared with PVC. TGA-FTIR indicated the reason why the low thermal stability of internally plasticized PVC was due to the instability of azide group. PVC material modified with castor oil based internal plasticizer has already shown great potential to replace the traditional PVC material in these products with high migration resistance requirements. Therefore, it was expected that the obtained internally PVC materials could be used as a bio-based alternative plasticizer for producing these PVC products such as food packing, toys and medical derives. However, the low thermal stability of the internally plasticized PVC material limits its use in wire and cable materials.

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REFERENCES

1. Y. Zhou, N. Yang and S. Hu, *Resour. Conserv. Recycl.*, **73**, 33 (2013).
2. Z. Qiu and P. Zhou, *RSC Adv.*, **4**, 51411 (2014).
3. P. Jia, M. Zhang, L. Hu, J. Zhou, G. Feng and Y. Zhou, *Polym. Degrad. Stab.*, **121**, 292 (2015).
4. M. G. A. Vieira, M. A. da Silva, L. O. dos Santos and M. M. Beppu, *Eur. Polym. J.*, **47**, 254 (2011).
5. M. Rahman and C. S. Brazel, *Prog. Polym. Sci.*, **29**, 1223 (2004).
6. P. Jia, M. Zhang, L. Hu and Y. Zhou, *Korean J. Chem. Eng.*, **33**, 1080 (2016).
7. S. Benjamin, E. Masai, N. Kamimura, K. Takahashi, R. C. Anderson and P. A. Faisal, *J. Hazard. Mater.*, **340**, 360 (2017).
8. A. L. Perez, M. Liong, K. Plotkin, K. P. Rickabaugh and D. J. Paustenbach, *Chemosphere*, **167**, 541 (2017).
9. J. H. Li and Y. C. Ko, *Kaohsiung J. Med. Sci.*, **28**, S17 (2012).
10. K. M. Gani, V. K. Tyagi and A. A. Kazmi, *Environ. Sci. Pollut. R.*, **24**, 17267 (2017).
11. P. Jia, M. Zhang, L. Hu, G. Feng, C. Bo and Y. Zhou, *ACS. Sustain. Chem. Eng.*, **3**, 2187 (2015).
12. J. Chen, X. Li, Y. Wang, K. Li, J. Huang, J. Jiang and X. Nie, *J. Taiwan Inst. Chem. E.*, **65**, 488 (2016).
13. P. Jia, M. Zhang, C. Liu, L. Hu, G. Feng, C. Bo and Y. Zhou, *RSC Adv.*, **5**, 41169 (2015).

14. B. W. Chieng, N. A. Ibrahim, Y. Y. Then and Y. Y. Loo, *Polymers*, **9**, 204 (2017).
15. M. P. Arrieta, M. D. Samper, M. Jiménez-López, M. Aldas and J. López, *Ind. Crop. Prod.*, **99**, 196 (2017).
16. D. T. C. Ang, Y. K. Khong and S. N. Gan, *J. Vinyl. Addit. Techn.*, **22**, 80 (2016).
17. S. Lee, M. S. Park, J. Shin and Y. W. Kim, *Polym. Degrad. Stab.*, **147**, 1 (2018).
18. P. Jia, L. Hu, X. Yang, M. Zhang, Q. Shang and Y. Zhou, *RSC Adv.*, **7**, 30101 (2017).
19. P. Jia, M. Zhang, L. Hu, F. Song, G. Feng and Y. Zhou, *SCI REP-UK*, **8**, 1589 (2018).
20. P. Jia, M. Zhang, L. Hu, R. Wang, C. Sun and Y. Zhou, *Polymers*, **9**, 621 (2017).
21. P. Jia, L. Hu, M. Zhang, G. Feng and Y. Zhou, *Eur. Polym. J.*, **87**, 209 (2017).
22. R. Navarro, M. P. Perrino, C. García, C. Elvira, A. Gallardo and H. Reinecke, *Macromolecules*, **49**, 2224 (2016).
23. K. W. Lee, J. W. Chung and S. Y. Kwak, *Macromol. Rapid Commun.*, **37**, 2045 (2016).
24. J. Choi and S. Y. Kwak, *Environ. Sci. Technol.*, **41**, 3763 (2007).
25. B. Y. Yu, J. W. Chung and S. Y. Kwak, *Environ. Sci. Technol.*, **42**, 7522 (2008).
26. W. Choi, J. W. Chung and S. Y. Kwak, *ACS Appl. Mater. Interfaces*, **6**, 11118 (2014).
27. C. Liu, J. Li, W. Lei and Y. Zhou, *Ind. Crop. Prod.*, **52**, 329 (2014).
28. L. Zhang, M. Zhang, Y. Zhou and L. Hu, *Polym. Degrad. Stab.*, **98**, 2784 (2013).
29. P. Jia, L. Hu, M. Zhang and Y. Zhou, *J. Therm. Anal. Calorim.*, **124**, 1331 (2016).
30. P. Jia, R. Wang, L. Hu, M. Zhang and Y. Zhou, *Pol. J. Chem. Technol.*, **19**, 16 (2017).
31. J. Lafarge, N. Kebir, D. Schapman, V. Gadenne and F. Burel, *Cellulose*, **20**, 2779 (2013).
32. B. Kiskan, G. Demiray and Y. Yagci, *J. Polym. Sci. Pol. Chem.*, **46**, 3512 (2008).
33. H. Qu, X. Liu, J. Xu, H. Ma, Y. Jiao and J. Xie, *Ind. Eng. Chem. Res.*, **53**, 8476 (2014).
34. S. V. Levchik and E. D. Weil, *Polym. Adv. Technol.*, **15**, 691 (2004).
35. A. I. Balabanovich, T. A. Zevaco and W. Schnabel, *Macromol. Mater. Eng.*, **289**, 181 (2004).
36. A. I. Balabanovich, *Thermochim. Acta*, **435**, 188 (2005).