

## Synthesis and characterization of novel pentaerythritol ester as PVC plasticizer

Yigang Wang,<sup>1,2</sup> Xiaoan Nie,<sup>1,2</sup> Xiaoying Li<sup>1,2</sup>

<sup>1</sup>Institute of Chemical Industry of Forest Products, National Engineering Laboratory for Biomass Chemical Utilization, Key and Open Laboratory on Forest Chemical Engineering, Key Laboratory of Biomass Energy and Material, Nanjing, Jiangsu Province 210042, China

<sup>2</sup>Institute of New Technology of Forestry, CAF, Beijing 100091, China

Correspondence to: X. Nie (E-mail: niexiaoan@126.com)

**ABSTRACT:** A novel bio-based PVC plasticizer, levulinic acid pentaerythritol ketal ester (LAPKE), was synthesized and evaluated as renewable resource alternatives to traditional phthalate. The structure of LAPKE was characterized by FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. The LAPKE and dioctyl phthalate (DOP) at different mass ratio were added to the PVC to prepare PVC samples. The mechanical properties of PVC samples at mass ratio of 1:1 showed that its tensile strength, elongation at break was up to an optimum value. The thermal stability was measured by dynamic thermal stability and thermogravimetric analysis (TGA), and the results showed that the thermal ability of PVC was improved with the addition of LAPKE. The weight loss of migration property (volatility, leaching test and exudation) has also increased by increasing mass ratio of LAPKE. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44227.

**KEYWORDS:** plasticizer; resins; structure-property relationships; thermoplastics

Received 12 June 2016; accepted 22 July 2016

DOI: 10.1002/app.44227

### INTRODUCTION

Poly(vinyl chloride) (PVC), one of the most versatile thermoplastics with wide utility, plays an important role in the plastic industry.<sup>1,2</sup> PVC can be used in military, construction, biomedical, baby-care, and food packing application, mainly because of the presence of plasticizers.<sup>3</sup> During the last decade, phthalate esters accounted for more than 80% of all the PVC plasticizers due to its good performance and low cost.<sup>4</sup> A review summarizes some study results on the migration of phthalate esters from PVC to different environments such as soil, marine ecosystem, indoor air, etc.<sup>5–7</sup> Studies show that the phthalate esters from the air can penetrate human skin rapidly.<sup>8,9</sup> Since 1999, the phthalate esters plasticizers have been forbidden to be used in the toys played by the children under the age of three.

Recently, no-toxic, environment and renewable materials for PVC plasticizers have drawn more attentions. As a versatile platform compound, levulinic acid is identified as the one of the 12 top value-added chemicals from biomass with numerous industry applications due to its high reactive keto and carboxyl groups.<sup>10,11</sup> These two functional groups make levulinic acid a potentially versatile building block for preparation of organic chemicals.<sup>12,13</sup> Most importantly, as a bio-based material, levulinic acid can be prepared from biomass such as glucose, 5-hydroxymethylfurfural, cellulose, miscanthus, and so on.<sup>14–17</sup>

In this study, a novel green PVC plasticizer, levulinic acid pentaerythritol ketal ester (LAPKE), was synthesized shown in Scheme 1. Our aim is to develop an efficient green PVC plasticizer that can be completely or partially replace the traditional DOP plasticizer. And meanwhile, the mechanical property, thermal stability and migration stability of PVC samples can also be improved.

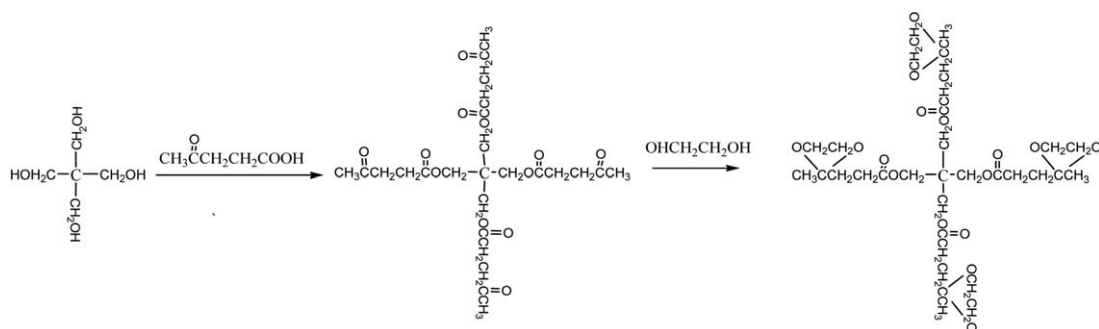
### EXPERIMENTAL

#### Materials

Levulinic acid and pentaerythritol were obtained from Aladdin Industrial Co., Ltd. Ethanediol was purchased from Nanjing Chemical Reagent Co., Ltd. Para-toluenesulfonic and cyclohexane were supplied by the Sinopharm Chemical Reagent Co., Ltd. The catalyst Qs-6 was obtained from Nanjing Jinling Petrochemical Research Institute Co., Ltd.

#### Synthesis

Hundred grams of pentaerythritol and 350 g levulinic acid were mixed in a four-necked round-bottom flask with a mechanical stirrer, condenser pipe and thermometer. The mixture was slowly heated to 90 °C. And as the mixture was melted, 0.45 g catalyst Qs-6 was added to the mixture. The mixture was further heated to 185 °C and remained for 5 h. In order to get rid of the generated water and unreacted excess levulinic acid, the



**Scheme 1.** The reaction scheme for the synthesis of LAPKE.

mixture was treated under 3 to 5 Torr caused by a vacuum pump. After the mixture was cooled to temperature, 183 g ethane-1,2-diol and 20 mL water-carrying agent, cyclohexane, were added. The reaction was allowed to continue at 85 °C for 4 h. Finally, cyclohexane was removed by reduced pressure distillation at 85 °C.

#### Preparation of PVC Specimens

DOP and LAPKE at different weight ratio were added to the PVC, and the formula was shown in Table I. The PVC specimens were prepared as followed<sup>18</sup>: firstly, the plasticizers and stabilizers were added to the PVC powder, and the blends were mixed by a mechanical mixer. Secondly, the mixtures were plasticized at 165 °C for 3 min by double-roller blending rolls (SY-6215-A1, Shiyuan Precision Instruments Co., Ltd of Dongguan, China), and its roll spacing was set at 2 mm. Thirdly, the specimens were made by hot press (XDY-1003, Shenzhen Chuangjiahong Machinery Co., Ltd, China) at 170 °C for 5 min. Finally, the thin films were made by a mould to a standard dumbbell shaped specimens.

#### Characterizations

**FT-IR.** FT-IR spectra of LA LAPE and LAPKE were obtained on a Nicolet iS10 FT-IR (Nicolet Instrument). The sample was scanned 32 times from 4000 to 400 cm<sup>-1</sup> with a resolution of 4.

**<sup>1</sup>H NMR and <sup>13</sup>C NMR.** The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of LAPKE dissolved in deuterated chloroform were recorded by a Bruker 400 MHz spectrometer (Bruker Instrument, Germany) at room temperature.

**Dynamic Mechanical Analysis (DMA).** The dynamic mechanical analysis (DMA) was performed via a DMTA Q800 (TA Instrument). The size of sample was 40 mm (*L*) ± 6 mm (*W*)

× 0.2 mm (*T*). The oscillatory frequency of the dynamic test was 1 Hz. The temperature was raised at a rate of 3 °C min<sup>-1</sup> at -50 to 150 °C.

**Thermogravimetric Analysis (TGA).** Thermogravimetric analysis (TGA) was carried out on a TG209F1 TGA thermal analysis instrument (Netzsch Instrument Crop., German). Each sample was scanned in N<sub>2</sub> atmosphere (50 mL/min) at the temperature of ambient temperature to 800 °C at a heating rate of 20 °C/min.

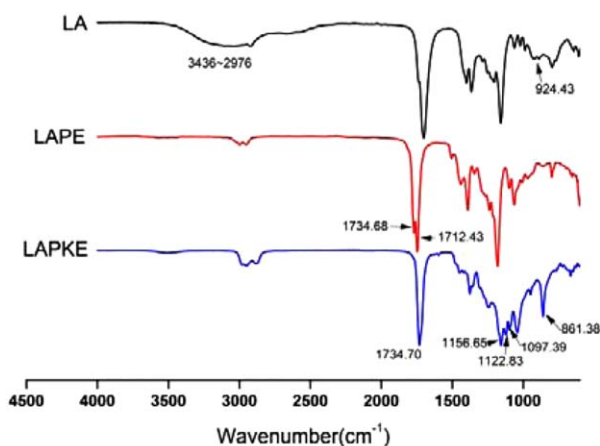
**Tensile Test.** The elongation at Break, tensile strength Young's modulus of samples was measured according to the GB/T 1040.1-2006. The test temperature was fixed at 20 °C, and the cross-head was set at 20 mm/min.

**Volatility.** The volatility test was measured according to the ISO 176:2005 plastics-determination of loss of plasticizers-activated carbon method. In this volatility test, the specimen size was 60 mm × 60 mm × 2 mm. Weigh the original specimen. Place specimen on the bottom of metal container and spread about 120 cm<sup>3</sup> of activated carbon over this specimen. And then put the lid on the container. Place the container in the oven controlled at a temperature of 70 ± 1 °C. After 24 h, remove the container from the oven and allow it to cool at room temperature. Remove the specimens from the container and carefully brush them free from any trace of carbon particles. Finally, reweigh the specimen after the volatility test.

**Leaching Test.** The leaching test was carried out according to ASTM D 1239-98. The preferred specimen size in this standard was 60 mm × 60 mm × 2 mm. The PVC specimens were immersed in different solvents (distill water, olive oil, 10% ethanol (v/v), 30% acetic acid (w/v), and petroleum ether) at a temperature of 23 ± 1 °C and a relative humidity of 50 ± 5% for

**Table I.** The Formulation of the PVC Specimens

Samples	PVC (g)	DOP (g)	LAPKE (g)	Calcium stearate (g)	Calcium stearate (g)
PVC 0	100	0	0	1.5	0.5
PVC 1	100	30	0	1.5	0.5
PVC 2	100	24	6	1.5	0.5
PVC 3	100	15	15	1.5	0.5
PVC 4	100	6	24	1.5	0.5
PVC 5	100	0	30	1.5	0.5



**Figure 1.** FT-IR spectra of products. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

24 h. After that the solvent extracted PVC specimens were rinsed and dried under the test conditions in oven at 30 °C for 24 h.

**Exudation.** In exudation test, the method was according to ASTM D2199-82. The PVC samples were cut to the size of 60 mm × 60 mm × 2 mm. The samples were placed between two sheets of unplasticized polyethylene terephthalate. The three sheets were pressed closely at the temperature of 30 °C for 72 h. Finally, the PVC samples were washed with water and dried.

**Dynamic Thermal Stability.** The dynamic thermal stability was measured by the torque rheometer according to the ASTM D 2538-02. The testing temperature was fixed at 180 °C, and rotor speed was maintained at 30 r/min.

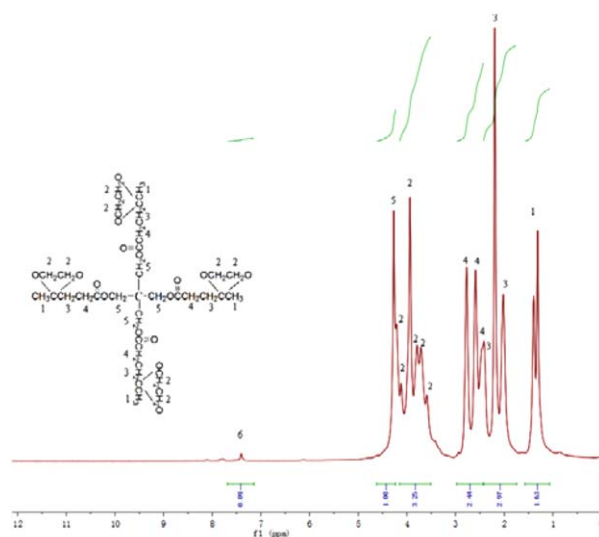
## RESULTS AND DISCUSSION

### FT-IR

Chemical structure of levulinic acid (LA), levulinic acid pentaerythritol ester (LAPE), and levulinic acid pentaerythritol ketal ester (LAPKE) were monitored by FT-IR. The spectrum of the products was depicted in Figure 1. The wide absorption peaks at 3436 to 2976  $\text{cm}^{-1}$  and around 924.43  $\text{cm}^{-1}$  belong to the  $\text{—OH}$  stretching vibration in the structure of carboxyl. The characteristic peak at 1712.43  $\text{cm}^{-1}$  was assigned to the absorption of  $\text{C=O}$  in the structure of ketone, and at 1734.68  $\text{cm}^{-1}$  it was also assigned to the absorption of  $\text{C=O}$ , but it was in the structure of ester. It can be seen that in the FT-IR spectra of LAPKE the absorption peak at 1712.43  $\text{cm}^{-1}$  disappeared. Moreover, three vibrational coupling characteristic peaks appeared at 1156.65, 1122.83, and 1097.39  $\text{cm}^{-1}$ , which were due to the form of  $\text{—C—O—C—O—C—}$  through ketal reaction. The absorption at 861.38  $\text{cm}^{-1}$  was observed due to the vibration of  $\text{—C—O—C—}$ .

### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR

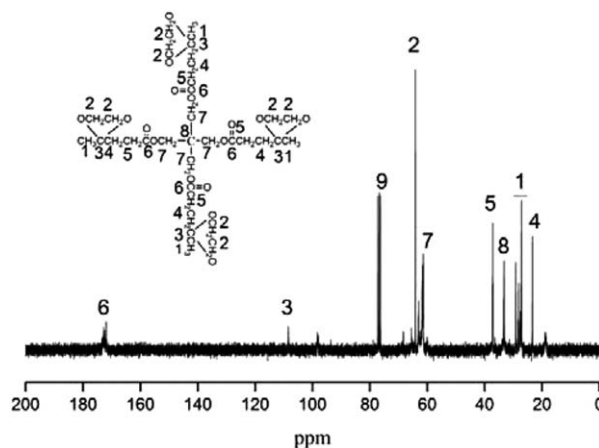
The molecular structure of LAPKE was also confirmed by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The  $^1\text{H}$  NMR spectra of LAPKE was shown in Figure 2. As indicated the peak at 1.3 ppm was corresponding to the terminal methyl protons ( $\text{—CH}_3$ ). The peaks located in region 3.5 to 4.2 ppm in this spectra exhibit the methylene protons ( $\text{—O—CH}_2\text{—CH}_2\text{—O—}$ ) in the five-



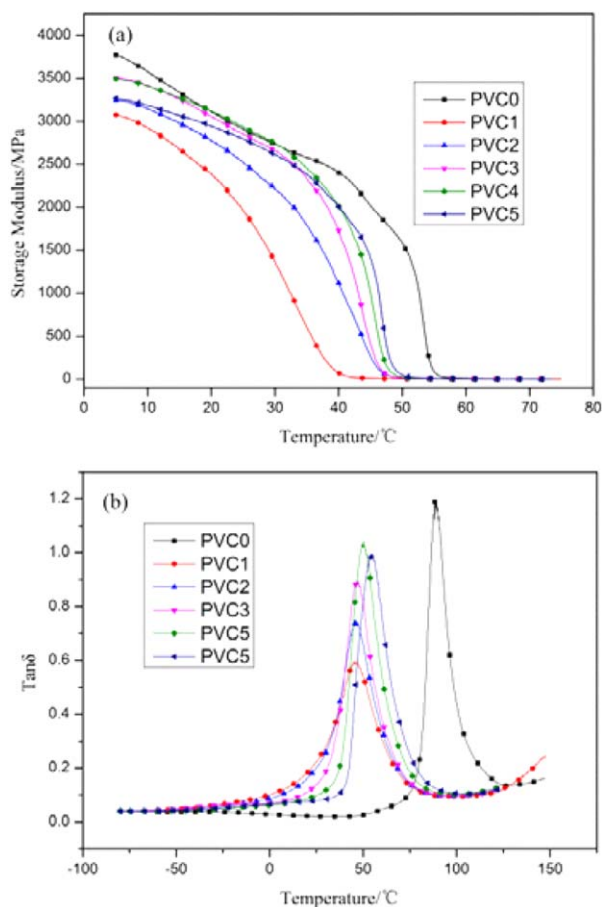
**Figure 2.**  $^1\text{H}$  NMR spectra of LAPKE. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

membered ring structure formed by ketal reaction. However, the methylene protons in the structure of  $\text{—C—CH}_2\text{—CH}_2\text{—C—}$  were at the ranges of 2.0 to 2.3 ppm and 2.4 to 2.7 ppm. Because of the spinspin splitting, a sextet peak and two triplet peaks occurred at 3.5 to 4.2, 2.0 to 2.3, and 2.4 to 2.7 ppm, respectively. And another methylene proton in the structure of  $\text{—C—CH}_2\text{—O—}$  was assigned at 4.3 ppm. The peak at 7.3 ppm was corresponding to proton of deuterated chloroform.

Figure 3 displayed the  $^{13}\text{C}$  NMR spectra of LAPKE. The peaks at around 28.3 ppm were methyl carbon ( $\text{—CH}_3$ ). The methylene carbons in the structure of  $\text{—C—CH}_2\text{—CH}_2\text{—C—}$  were at 37.3 ppm and 23.4 ppm, respectively. The methylene carbon in the structure of  $\text{—O—CH}_2\text{—CH}_2\text{—O—}$  in the five-membered ring structure were at 63.0 ppm. And another methylene carbon ( $\text{—C—CH}_2\text{—O—}$ ) was at 61.4 ppm. The peak at 108.4 and 33.4 ppm were corresponding to the central carbon in the structure of  $\text{—C—C—C—}$  and  $\text{—C—C—C—}$ . The peak at 172.2 ppm was corresponding



**Figure 3.**  $^{13}\text{C}$  NMR spectra of LAPKE.



**Figure 4.** The DMA curves of different PVC blends. (a) Describes the change of storage modulus as the temperature increased. (b) Is the change of  $\text{Tan } \delta$  at the temperature from  $-80^\circ\text{C}$  to  $150^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

to the carbonyl carbon in the ester group. The peaks at 76.8 ppm referred to the carbon of deuterated chloroform.

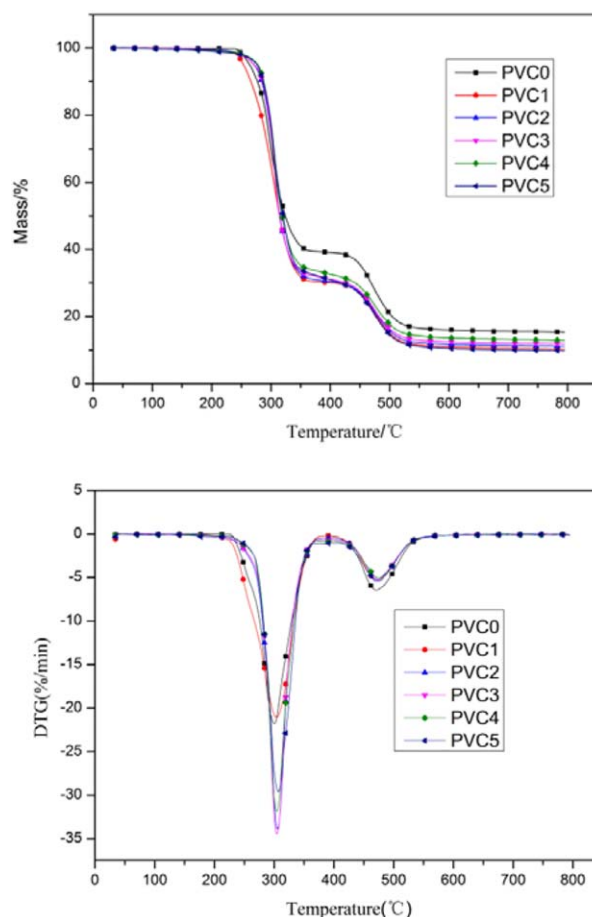
#### Dynamic Mechanical Analysis (DMA)

DMA was a usual measurement in viscoelastic properties, including the storage modulus and  $\text{Tan } \delta$  changing with the temperature. The changes in storage modulus values with temperature were shown in Figure 4(a). The storage modulus of PVC without plasticizers was the highest among all the PVC blends at the same temperature, and the storage modulus decreased with the addition of plasticizers, especially with the increasing mass ratio of DOP. A significant decrease of storage modulus occurred at lower temperature. The glass transition temperature ( $T_g$ ) was an important metrics to measure the plasticizing efficiency of plasticizers. The results were shown in Figure 4(b). From Figure 4(b) only one peak was seen at every curve, which indicated that the plasticizer had a good compatibility with the PVC. The  $T_g$  of PVC0, PVC1, PVC2, PVC3, PVC4, PVC5 were  $89.01^\circ\text{C}$ ,  $45.14^\circ\text{C}$ ,  $46.37^\circ\text{C}$ ,  $46.59^\circ\text{C}$ ,  $50.01^\circ\text{C}$ , and  $54.25^\circ\text{C}$ . According to the free volume theory of plasticization, the low molecular had the ability to reduce the force between the PVC chains and lubricate the PVC chains. It was worth noting that in the structure of

LAPKE, there was the presence of  $-\text{C}-\text{O}-\text{C}-\text{O}-\text{C}-$ , which can form the hydrogen bonds between the plasticizer and the PVC chains. The forces of PVC chains were further weakened. Combined the storage modulus and  $T_g$ , good viscoelastic properties were obtained when the mass ratio of LAPKE was controlled below 50%.

#### Thermogravimetric Analysis (TGA)

The thermal stability of PVC samples were evaluated by TGA analysis under the air at the heating rate of  $20^\circ\text{C}/\text{min}$ . The TG and DTG curves of different PVC specimens were shown in Figure 5, and the analysis data was shown in Table II. It can be seen from TGA curve that there was a two-stage thermal degradation process. The first stage was at  $200$  to  $350^\circ\text{C}$ , which was corresponding to the dechlorination of PVC including the formation and stoichiometric elimination of HCl.<sup>19</sup> The second stage at the temperature of  $420$  to  $550^\circ\text{C}$  was contributed to the degradation of complex structure such as the cross linking, cyclization, and splitting of chains, and aromatization.<sup>20–22</sup> Usually, the onset of degradation temperature referred to the temperature at which the weight loss was up to 5%.<sup>23</sup> The thermal degradation parameters of PVC samples were given in Table II.



**Figure 5.** The TGA and DTG curves of PVC specimens. The TGA curves show the mass change of specimens from room temperature to  $800^\circ\text{C}$ . The DTG curves show the mass loss rate change from room temperature to  $800^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Table II.** The Thermal Degradation Parameters of PVC Specimens

Samples	PVC0	PVC1	PVC2	PVC3	PVC4	PVC5
$T_{\text{onset } 5\%}^a$ (°C)	263.8	253.6	271.5	272.1	276.6	277.1
$T_{\text{max}}^b$ (°C)	300.2	303.9	305.4	304.5	304.4	306.8

<sup>a</sup>The temperature at which the PVC samples lose 5 wt %.

<sup>b</sup>The peak temperature of DTG at which it is the maximum degradation rate.

As the increase of LAPKE plasticizer, the onset of degradation temperature increased from 253.6 °C to 277.1 °C. It can be concluded that the addition of LAPKE improved the stability of PVC samples. However, compared with the  $T_{\text{onset } 5\%}$  of none plasticized PVC, the onset of degradation temperature of PVC plasticized by DOP decreased from 263.8 °C to 253.6 °C.  $T_{\text{max}}$  referred to the temperature that was the maximum degradation rate. Clearly, an increase in LAPKE content generally resulted in higher  $T_{\text{max}}$  values from 300.2 °C to 306.8 °C. In conclusion, the presence of LAPKE can improve the thermal stability, and as the mass ratio increase of LAPKE and DOP, the  $T_{\text{onset } 5\%}$  and  $T_{\text{max}}$  became higher.

### Tensile Properties

Mechanical properties are important index to evaluate the plasticizing effect of plasticizer for PVC. The values of tensile strength, percent elongation, modulus of elasticity, and shore hardness of obtained plasticized PVC samples are shown in Table III. It can be seen that the addition of plasticizer efficiency increased the elongation at break, but the tensile strength, modulus of elasticity, and shore hardness decreased. Compared PVC 1 and PVC 5, the elongation at break of PVC 1 was a little higher, but the tensile strength, modulus of elasticity and shore hardness were a little lower. It was worth noting that the highest value of the elongation at break was the sample of PVC 3, and combined with its other mechanical properties values in Table III, it could be concluded that the efficient plasticizer was the mixture of DOP and LAPKE at mass ratio of 1:1. On the other hand, the molecular structure of LAPKE can be considered as four branches occurred from the central carbon atoms like microspheres, which can reduce the interactions between PVC molecular. Meanwhile, the abundant presence of many oxygen atoms in the LAPKE enhanced the intermolecular forces between LAPKE and PVC through hydrogen bond. Therefore, compared with the pure DOP, the tensile strength, modulus and elasticity and shore hardness of pure LAPKE plasticized PVC was higher.

**Table III.** Mechanical Properties of PVC Specimens

Samples	Elongation at break (%)	Tensile strength (MPa)	Modulus of elasticity (MPa)	Shore hardness(HD)
PVC 0	118	40	1076	62.5
PVC 1	357	19	80	42.3
PVC 2	351	31	121	45.6
PVC 3	372	33	97	45.1
PVC 4	347	32	162	47.6
PVC 5	332	35	241	48.7

**Table IV.** The Volatility and Exudation Properties of PVC Specimens

Samples	PVC1 (%)	PVC2 (%)	PVC3 (%)	PVC4 (%)	PVC5 (%)
Volatility	1.819	1.663	1.337	1.025	0.952
Exudation	0.011	0.009	0.012	0.015	0.010

### Migration Stability

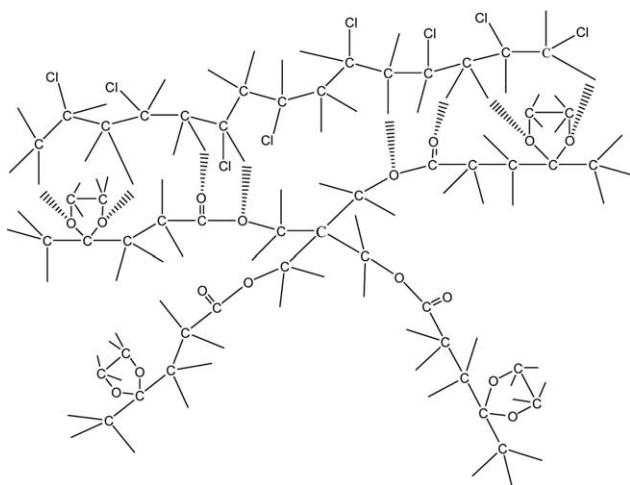
Migration was an important behavior during the use of plasticizer in polymers. Specially, it was dangerous when the plasticizer was added to the baby nipple. According to the environments where the PVC products were used, the migration stability was characterized by the amount of plasticizer migrated out of the PVC samples to the gaseous phase (volatility), liquid phase (leaching test), and solid substrates (exudation) to determine the degree of plasticizer migration. The weight losses were determined by the weight before and after the tests, and the formula was as follows:

$$\text{Weight loss of plasticizers (\%)} = (W_{\text{before}} - W_{\text{after}}) / W_{\text{before}}$$

where  $W_{\text{before}}$  and  $W_{\text{after}}$  are the weights of PVC samples before and after the tests.

The research had found that the volatility, exudation and leaching test process depended on the compatibility between the plasticizers and PVC, the polarity and structure of plasticizer, temperature, the surrounding media, and other conditions.<sup>24</sup> If the PVC samples were under the same condition, the most important influence factor on the migration was the structure and its compatibility with PVC. Table IV was the volatility and exudation properties of different PVC samples, it can be seen that the volatilization loss decreased in the samples according to the following order: PVC1, PVC2, PVC3, PVC4, and PVC5. Figure 6 showed the possible hydrogen bond between the PVC chain and two chains of LAPKE molecule. Compared with interaction between the DOP and the PVC, it had stronger intermolecular forces between the PVC chain and LAPKE molecule. So the volatility weight loss decreased as the LAPKE increased. In the exudation, there was no significant difference and mass loss during the experimental period among those samples, indicating that the plasticizers were compatible with PVC and could not be extracted easily.

The leaching test was operated through the plasticized PVC immersed distill water, olive oil, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether at a temperature of  $23 \pm 1$  °C



**Figure 6.** The possible hydrogen bonds between the PVC chain and two chains of LAPKE molecule.

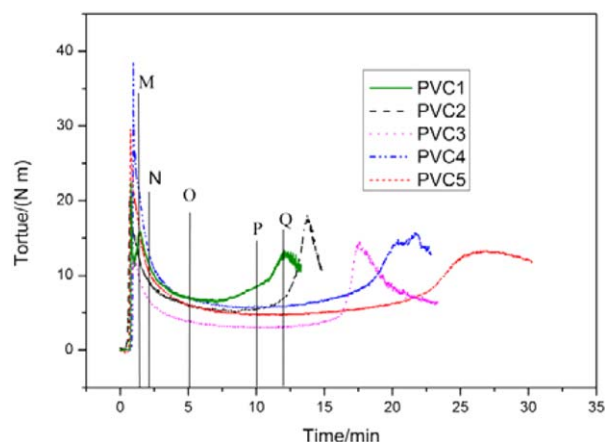
for 24 h. And the results were shown in Table V. To each sample, the order of weight loss was as follows: petroleum ether, olive oil, 30% acetic acid, 10% ethanol, and water. The results indicated that the plasticized PVC had no significant weight loss (less than 1%) in aqueous environment. However, when the plasticized PVC samples were immersed in organic solvent, the weight loss increased. To different PVC samples, compared with pure DOP plasticized sample PVC1, the weight loss decreased gradually as the mass ratio in the PVC samples increased. These results can be attributed to the stronger intermolecular interaction and better compatibility between the PVC and the plasticizer of LAPKE. In conclusion, the presence of LAPKE can improve the resistance of exudation.

#### Dynamic Thermal Stability

Pure PVC can be easily decomposed to generate low molecular under high temperature conditions, which seriously limited its molding process and application. In this study, the dynamic thermal stability of PVC blends was measured through the torque rheometer. The important influence to the thermal stabilization time was chamber temperature and rotating speed. So in this study, the chamber temperature was fixed at 180 °C and the rotating speed was fixed at 30 r/min. The torque rheological curves of PVC blends were shown in Figure 7. In Figure 7 the points M, N, O, P, and Q referred to fusion torque, process of melting, balance torque, and starting point of degradation of PVC1 blends. According to the Figure 7, the thermal stabilization time, fusion torque and balance torque were shown in Table VI. It can be seen that the thermal stabilization time

**Table V.** Leaching Test Value of PVC Specimens

Samples	Water (%)	Olive oil (%)	10% Ethanol (%)	30% Acetic acid (%)	Petroleum ether (%)
PVC1	0.022	1.721	0.102	0.113	12.896
PVC2	0.019	1.014	0.075	0.099	13.241
PVC3	0.008	0.854	0.015	0.051	9.451
PVC4	0.005	0.571	0.010	0.045	6.741
PVC5	0.004	0.203	0.008	0.023	6.523



**Figure 7.** The torque rheological curve of PVC blends. The thermal stabilization time, fusion torque and balance torque can be measured at 180 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table VI.** The Thermal Stabilization Time, Fusion Torque, and Balance Torque of PVC Blends

Samples	PVC1	PVC2	PVC3	PVC4	PVC5
Thermal stabilization time	8.45	11.45	15.25	18.1	23.35
Fusion torque	15.9	20.5	29.6	38.6	27.5
Balance torque	6.8	5.4	3.1	5.8	4.8

increased from 8.45 to 23.35 min with the increasing mass ratio of LAPKE. It indicated that the addition of LAPKE can efficiently improve the thermal stabilization time. Compared the fusion torque with balance torque, they were not identical with the increasing mass ratio of LAPKE. With the increasing of mass ratio of LAPKE, the fusion torque of PVC samples were higher than PVC 1 blends, which mean that the melt viscosity may be increased and the PVC blends could not be benefit to the processing.<sup>25</sup> However, from balance torque we also can be seen that the values of balance torque after the addition of LAPKE were a little lower than that of PVC 1 blends. Low balance torque would be conducive to thermoplastic processing of PVC blends.

#### CONCLUSIONS

In this study, a novel bio-based plasticizer, LAPKE, was synthesized and blended with PVC to evaluate the performance of

PVC through partially or absolutely replacing the commercial plasticizer DOP. As the addition of LAPKE, although the glass transition temperature rise from 45.14 to 54.25 °C, the performance of PVC samples has been improved by the analysis of thermal stability (dynamic thermal stability,  $T_{\text{onset } 5\%}$  and  $T_{\text{max}}$ ), migration stability (volatility, leaching test, and exudation) and tensile properties (tensile strength, percent elongation, modulus of elasticity, and shore hardness). All the results could be attributed to stronger intermolecular forces between the PVC chain and LAPKE molecule.

#### ACKNOWLEDGMENTS

This work was financially supported by The National 12th Five year Science and Technology Support Plan of China (Grant Number: 2014BAD02B02).

#### REFERENCES

1. Vadukumpully, S.; Paul, J.; Mahanta, N.; Valiyaveetil, S. *Carbon* **2011**, *49*, 198.
2. Zhou, Y.; Yang, N.; Hu, S. *Resour. Conserv. Recycling* **2013**, *73*, 33.
3. Choi, J.; Kwak, S. Y. *Environ. Sci. Technol.* **2007**, *41*, 3763.
4. Choi, J. S.; Park, W. H. *Polym. Test.* **2004**, *23*, 455.
5. Clausen, P. A.; Hansen, V.; Gunnarsen, L.; Afshari, A.; Wolkoff, P. *Environ. Sci. Technol.* **2004**, *38*, 2531.
6. Di Gennaro, P.; Collina, E.; Franzetti, A.; Lasagni, M.; Luridiana, A.; Pitea, D.; Bestetti, G. *Environ. Sci. Technol.* **2005**, *39*, 325.
7. Mackintosh, C. E.; Maldonado, J. A.; Ikonou, M. G.; Gobas, F. A. P. C. *Environ. Sci. Technol.* **2006**, *40*, 3481.
8. Xu, Y.; Little, J. C. *Environ. Sci. Technol.* **2006**, *40*, 456.
9. Janjua, N. R.; Mortensen, G. K.; Andersson, A. M.; Kongshoj, B.; Wulf, H. C. *Environ. Sci. Technol.* **2007**, *41*, 5564.
10. Leonard, R. H. *Ind. Eng. Chem.* **1956**, *48*, 1330.
11. Bozell, J. J.; Moens, L.; Elliott, D. C.; Wang, Y.; Neuenschwander, G. G.; Fitzpatrick, S. W.; Bilski, R. J.; Jarnefeld, J. L. *Resour. Conserv. Recycling* **2000**, *28*, 227.
12. Kitano, M.; Tanimoto, F.; Okabayashi, M. *Chem. Econ. Eng. Rev.* **1975**, *7*, 25.
13. Thomas, J. J.; Barile, R. G. *Biomass Wastes* **1985**, *8*, 1461.
14. Girisuta, B.; Janssen, L. P. B. M.; Heeres, H. J. *Green Chem.* **2006**, *8*, 701.
15. Runge, T.; Zhang, C. *Ind. Eng. Chem. Res.* **2012**, *51*, 3265.
16. Weingarten, R.; Cho, J.; Xing, R.; Conner, W. C.; Huber, G. W. *ChemSusChem* **2012**, *5*, 1280.
17. Weingarten, R.; Conner, W. C.; Huber, G. W. *Energy Environ. Sci.* **2012**, *5*, 7559.
18. Chen, J.; Liu, Z.; Jiang, J.; Nie, X.; Zhou, Y.; Murray, R. E. *RSC Adv.* **2015**, *5*, 56171.
19. Semsarzadeh, M. A.; Mehrabzadeh, M.; Arabshahi, S. S. *Eur. Polym. J.* **2002**, *38*, 351.
20. Yao, Q.; Wilkie, C. A. *J. Vinyl Additive Technol.* **2001**, *7*, 26.
21. Li, J.; Ke, C.; Xu, L.; Wang, Y. *Polym. Degrad. Stab.* **2012**, *97*, 1107.
22. Pitchaimari, G.; Sarma, K. S. S.; Varshney, L.; Vijayakumar, C. T. *Thermochim. Acta* **2014**, *597*, 8.
23. Amaro, L. P.; Coiai, S.; Ciardelli, F.; Passaglia, E. *Waste Manage.* **2015**, *46*, 68.
24. Kovačić, T.; Mrklić, Ž. *Thermochim. Acta* **2002**, *381*, 49.
25. Jia, P.; Zhang, M.; Liu, C.; Hu, L.; Zhou, Y. H. *J. Appl. Polym. Sci.* **2015**, *132*, 1.