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Effect of chlorinated phosphate ester based on castor oil on thermal degradation of poly (vinyl chloride) blends and its flame retardant mechanism as secondary plasticizer

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A novel flame retardant chlorinated phosphate ester based on castor oil (CPECO) was synthesized. Chemical structure of CPECO was characterized with FTIR, ¹H NMR and ³¹P NMR. The application of CPECO as a secondary plasticizer for poly (vinyl chloride) (PVC) not only gained satisfied flame retardancy and mechanical properties, but also substituted for dioctyl phthalate (DOP) partly. Flame retardant properties of PVC plasticized with CPECO was explored with LOI tests, SEM, TGA, TGA-FTIR, TGA-MS and cone calorimeter tests. The results showed that LOI value of plasticized PVC blends could increase from 23.6 % to 35.4 %. TGA-FTIR and TGA-MS detected that the main pyrolysis products of PVC blends were H₂O, HCl, CO₂, CO and C₆H₆. Cone calorimeter tests showed that peak heat release (pHRR) of plasticized PVC blends could decrease from 379.00 to 289.00 kW/m², total heat release (THR) decreased from 31.78 to 19.12 MJ/m². The flame retardant mechanism of plasticized PVC blends could be concluded that phosphorous-containing components generated from pyrolysis of CPECO could promote formation of char residual. The char residual was blown by evolving gases which produced a foaming and expansion of the char layer. The carbonaceous char layer is effective to slow mass and heat transfer between the gas and condensed phases and to protect the underlying material from further combustion. The glass-transition temperature (T_g), mechanical properties of PVC blends and migration stability of CPECO were investigated.

1. Introduction

Poly(vinyl chloride) (PVC) materials are widely used in pipes, packaging, blood bags, children toys, wire and cable due to their excellent mechanical and physical properties.¹⁻² However, neat PVC can almost not be processed and utilized without plasticizers. In order to obtain the desired flexible and durable PVC products, large amount of plasticizers are usually mixed with PVC. At present, more than 500 kinds of plasticizers have been commercialized. The main commercial plasticizers are dioctyl phthalate (DOP) and dibutyl phthalate (DBP). 90% of plasticizers used in China are phthalate plasticizers.³ But these phthalates easily diffuse to surrounding and reduce performance of PVC products, the loss of plasticizer caused changes in the long-time properties of the PVC products.⁴⁻¹⁰ The plasticized PVC with DOP burns easily which restricts its application, especially in the field with high requirement of flame retardant properties such as wire and cable. One effective way to improve the flame retardancy of PVC materials is adding flame retardants such as antimony trioxide (Sb₂O₃), alumina trihydrate, Al(OH)₃,¹¹ and triphenyl phosphate, trimethyl phosphate, tris(chloropropyl) phosphate, Di-n-octylphenyl phosphate,¹² but the addition of flame retardants usually decreases the mechanical properties of PVC blends. It is necessary to prepare flame retardant PVC materials using flame retardant plasticizers

which could effectively improve the mechanical and flame retardant properties of PVC blends. Traditional intumescent flame retardant formulation is a blend of acid source, carbon source and gas sources. When the three parts are compounded appropriately, a synergistic flame retardant effect will be formed.¹³⁻¹⁴ So a plasticizer could supply acid source, carbon source and gas sources in the thermal degradation of PVC which will improve the flame retardancy of PVC products and expand the application range of PVC materials.

The raw materials of most of plasticizers are petroleum, scarcity of petroleum resources and the rising cost of petroleum products have led to the increasing trend towards developing of alternate sources of materials for industrial uses. In recent years, extensive work has been done to develop plasticizer from renewable resources. Some researchers have reported the synthesis and possible application of bio-based plasticizers such as cardanol-based plasticizer,¹⁵ epoxidized sunflower oil,¹⁶ epoxidized safflower oil,¹⁷ Low-Molecular-Weight glycerol esters,¹⁸ oleic acid polyester,¹⁹ rice fatty acid,¹ and epoxidized soybean oil.²⁰⁻²¹ Epoxidized soybean oil has been used as plasticizer of PVC for years, but the synthesis of soybean oil including flame retardant groups and the mechanism of flame retardant has never been reported. In our study, we look forward to preparing a novel bio-based plasticizer containing retardant groups based on castor oil, and partly to replace the phthalate as secondary plasticizer for PVC.

In this work, a novel flame retardant chlorinated phosphate ester based on castor oil (CPECO) has been synthesized. Its chemical structure was characterized with FTIR, ¹H NMR and ³¹P NMR. PVC blends plasticized with CPECO was prepared using tetrahydrofuran as solvent. The thermal and flame retardant properties of PVC blends were characterized with LOI tests, SEM, TGA, TGA-FTIR, TGA-MS and cone calorimeter tests. The flame

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retardant mechanism, mechanical properties and migration stability of PVC plasticized with CPECO was also explored. The objective of this work is to demonstrate that the novel flame retardant plasticizer derived from renewable resources castor oil can offer excellent flame retardancy and mechanical property for PVC and provide new ideas for development of vegetable-based-plasticizer.

2. Experimental

2.1 Materials

Castor oil (CO), phosphate, phosphorus oxychloride, dioctyl phthalate (DOP) and glacial acetic acid were obtained from Nanjing Chemical Reagent Co., Ltd. Hydrogen peroxide; aluminum chloride and methylbenzene were supplied by Aladdin Chemical Co., Ltd. Polyvinyl chloride (PVC) was supplied by Hanwha (South Korea) with K value 65.0 and degree of polymerization 1300 ± 100 .

2.2 Synthesis

2.2.1 Synthesis of castor oil polyol ester (COPE). 100 g of castor oil and 100 g of acetic anhydride was mixed in a three-necked round-bottom flask which was equipped with a mechanical stirrer, condenser pipe and thermometer. Stir at 140 °C for 1 h to finish esterification. Then the reaction mixture was washed 3 times with distilled water and removed the water with a rotary evaporator at 60 °C.

2.2.2 Synthesis of epoxidized castor oil polyol ester (ECOPE). 100 g of COPE, 10 g of glacial acetic acid and 0.5 g of concentrated phosphoric acid was mixed in a four-necked round-bottom flask which was equipped with a mechanical stirrer, condenser pipe, thermometer and constant pressure funnel. 60 ml of hydrogen peroxide solution was dropped in the reaction in 30 min and stirred at 60 °C for 8 h to finish epoxidation reaction. Then the reaction mixture was separated from water with separating funnel and washed 3 times with distilled water, then removed the water with a rotary evaporator at 60 °C. The chemical reaction process of ECOPE was shown in Fig. 1.

2.2.3 Synthesis of chlorinated phosphate ester based on castor oil (CPECO). 15.3 g of phosphorus oxychloride and 0.15 g of aluminum chloride was mixed in a four-necked round-bottom flask which was equipped with a mechanical stirrer, gas collection device, thermometer and constant pressure funnel. 100 g of ECOPE was dropped in the reaction in 30 min and stirred at 60 °C for 3 h to finish the reaction. Then the reaction mixture was separated from water with separating funnel and washed 3 times with distilled water, then removed the water with a rotary evaporator at 60 °C. The chemical reaction process of CPECO was shown in Fig. 1.

2.2.4 Preparation of PVC blends. PVC was mixed with CPECO and DOP at different weight ratio of PVC/ CPECO /DOP (100/40/0, 100/35/5, 100/30/10 and 100/20/20) using THF as the solvent. The mixture was thoroughly agitated by mechanical stirring for 1 h followed by sonication for 10min. The samples were then cast into Petri dishes (diameter 19 cm) and dried at ambient temperature for 7 days to remove traces of residual solvent and to obtain thin films.¹⁵ The composition of PVC films was showed in Table 1.

2.3 Characterizations

FT-IR spectra of CO and CPECO were recorded on a Nicolet iS10 FT-IR (Nicolet Instrument Crop., USA) Fourier transformed infrared spectrophotometer. The spectra were acquired in the range of 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1} .

¹H NMR spectra of CO and CPECO were recorded by using an AV-300 NMR spectrometer (Bruker, Germany) at a frequency of 400 MHz with

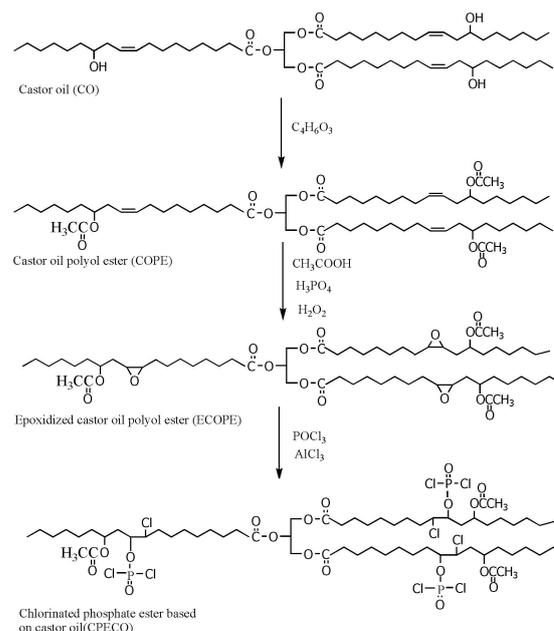


Fig.1 The idealized reaction scheme for the synthesis of CPECO

tetramethylsilane as an internal standard and deuterated chloroform (CDCl_3) as solvent.

Phosphorus nuclear magnetic resonance (³¹P NMR) spectra for the plasticizers based on castor oil were recorded on an AV-300 instrument with tetramethylsilane as an internal standard as reference and d_6 -DMSO as solvent.

The LOI values were measured on a JF-3 oxygen index measuring instrument (Nanjing Lei instrument Co. Ltd., China) according to the standard of Plastics-Determination of burning behavior by oxygen index (GB/T 2406.1-2008, China).

The carbon layer of PVC films after LOI tests were investigated with a Hitachi 3400-1 (Hitachi, Japan) scanning electron microscope instrument, operated at 12kV. The fracture of all surfaces was sputtered with gold to avoid electrostatic charging during examination.

TGA was carried out in a TG209F1 TG thermal analysis instrument (Netzsch Instrument Crop., German) in N_2 atmosphere ($50 \text{ ml} \cdot \text{min}^{-1}$) at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$. The samples were measured in a platinum pan with a mass of about 5 mg and scanned from 40 °C to 800 °C.

The TGA-FTIR measurements were carried out using a 409PC thermal analyzer (Netzsch, Germany) coupled with a Nicolet iS10 FT-IR (Nicolet Instrument Crop., USA). About 10 mg of each sample was heated from 40 °C to 800 °C at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 . The spectra were acquired in the range of 4000 cm^{-1} to 500 cm^{-1} at a resolution of 4 cm^{-1} .

The TGA-MS measurements were carried out using a 409PC thermal analyzer (Netzsch, Germany) coupled with a QMS403C instrument (Netzsch, Germany). About 10 mg of each sample was heated from 40 °C to 800 °C at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere. Mass scanning was carried out over the range m/v 2-200.

The combustion properties were evaluated using a cone calorimeter. All samples ($100 \times 100 \times 2 \text{ mm}^3$) were exposed to a FTT200 cone calorimeter (FTT Instrument Crop., UK) under a heat flux of $35 \text{ kW} \cdot \text{m}^{-2}$ according to ISO-5660 standard procedures.

The dynamic mechanical analysis was performed via a DMTA Q800 (TA Instruments, US) with gas cooling accessory to observe the α -transitions of the PVC blends under investigation. Rectangular samples of geometry 60 mm (L) \times 10 mm (W) \times 4 mm (T). The oscillatory frequency of the dynamic test was 1 Hz. The temperature was raised at a rate of $3^\circ\text{C}/\text{min}$ in the range of -80°C - 100°C .

Tensile modulus, tensile strength, and elongation at break were determined according to GB/T 1040.1-2006 (China) under ambient conditions using E43.104 Universal Testing Machine (MTS Instrument Crop., China). The reported values were the average of 6 samples.

Leaching tests were based on ASTM D1239-98. The test conditions were restricted at a temperature of $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. The PVC specimens were immersed in five different solvents (distilled water, oil, etc.)

Table 1 The composition of PVC blends

Sample	PVC	DOP	CPECO
PVC0	100	0	0
PVC1	100	40	0
PVC2	100	35	5
PVC3	100	30	10
PVC4	100	20	20

oil, 10 % (v/v) ethanol, 30 % (w/v) acetic acid and petroleum ether). Samples were weight and kept in 200 mL of each solvent. After 24 h, the solvent extracted PVC specimens were rinsed and then wiped up. Afterward, all of the PVC specimens were dried under the test conditions in oven at 30 °C for 24 h and reweighed. The extraction loss was calculated according to the Equation 1. Equation 1: Weight loss = $[(W_1 - W_2) / W_1] \times 100$, where W_1 = initial weight of test specimen, and W_2 = final weight of test PVC specimen.²¹⁻²⁴

3 Results and discussion

3.1. FTIR

Chemical structure of CO, COPE, ECOPE and CPECO were monitored using FTIR. The FTIR spectrum of the products was depicted in Fig.2. From the FTIR spectrum of CO, some characteristic peaks were presented in the spectrum of CO, the absorption band at about 3372 cm⁻¹

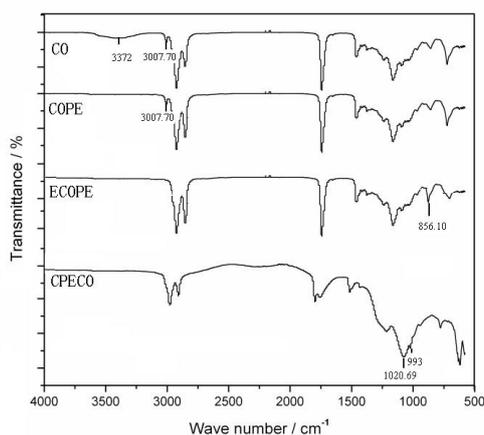


Fig.2 FTIR spectra of products

corresponding to hydroxyl groups connected to the fatty acid chains. The absorption at about 3007.70 cm⁻¹ corresponds to stretching vibration of double bands of CO. The absorption at about 2930 and 2962 cm⁻¹ was attributed the methyl and methylene groups. In the FTIR spectrum of COPE, the hydroxyl groups could not be found at around 3370 cm⁻¹, and the absorption at about 2930 cm⁻¹ become strong than that of CO, implying that esterification reaction of hydroxyl groups of CO with acetic anhydride occurred.

In the FTIR spectrum of ECOPE, the characteristic peak of epoxy group was observed at about 856.10 cm⁻¹, while the stretching vibration of double bands disappeared comparing to that of COPE, the results could be indicated that epoxidation reaction had occurred. The FTIR spectrum of CPECO was depicted in Fig. 2. The absorption band at about 856.10 cm⁻¹ of CPECO was almost vanished comparing to that of ECOPE, and a new absorption band appeared at about 993 and 1020.69 cm⁻¹ which assigned to the -P-O-C- groups, implying epoxy groups were expended in the formation of phosphate groups.²⁵⁻²⁶

3.2. ¹H NMR

The chemical structure of the products was monitored with ¹H NMR further. The ¹H NMR spectra of CO, COPE, ECOPE and CPECO were presented in Fig.3, Fig.4, Fig.5 and Fig.6 respectively. Fig. 3 presented the ¹H NMR spectrum of CO, the methyl protons were at $\delta=0.9$ ppm (peak 1). The fatty acid protons [(CH₂)_n-CO-] (peak 6) were at $\delta=2.35$ ppm. The methylene protons of glycerol were in the range of $\delta = 4.1 - 4.4$ ppm (peak 9). The methine protons of glycerol was at $\delta = 5.4$ ppm (peak 8), methyleneprotons attached to hydroxyl (-CH-OH) were in the range of $\delta=3.6$ ppm (peak 7), the peak at $\delta=5.6$ ppm (peak 10) was corresponding to the double bond protons (-CH=CH-) of fatty acid, while the peak $\delta=2.1$ ppm (peak 5) was assigned to -CH₂- of HO-C-CH₂-C=C- and the range of $\delta=1.4$ ppm (peak 2) was assigned to the other -CH₂-. Comparing to the ¹H NMR spectra of CO, a strong peak appeared at $\delta=0.9$ ppm in the ¹H-NMR spectra of COPE, implying that more methyl protons generated in the esterification than that of CO, and the hydroxyl groups could not be found at around 3370 cm⁻¹ in the FT-IR spectrum of COPE. Both the ¹H-NMR spectra

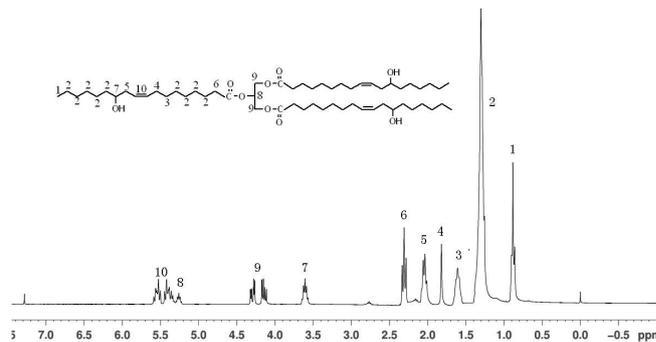


Fig.3 ¹H NMR spectrum of castor oil

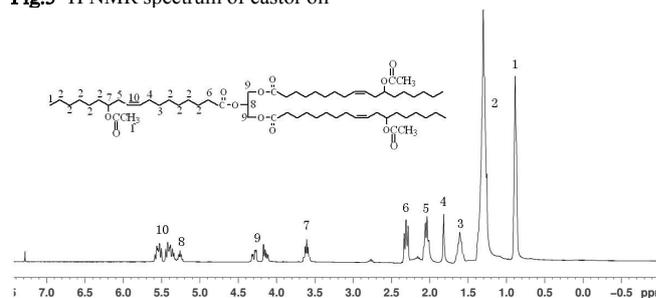


Fig.4 ¹H NMR spectrum of COPE

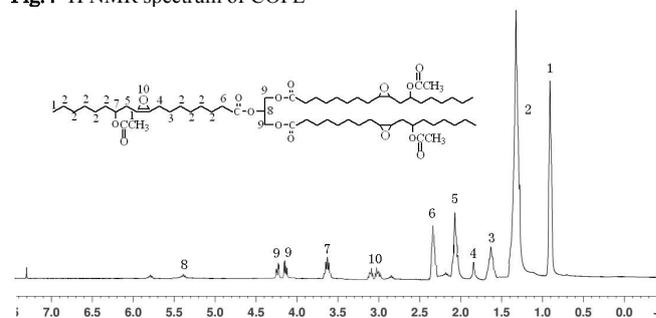


Fig.5 ¹H NMR spectrum of ECOPE

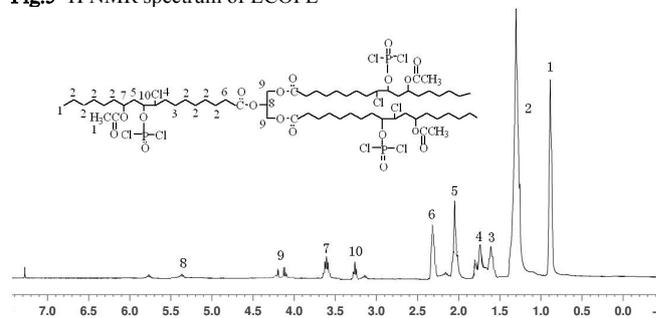
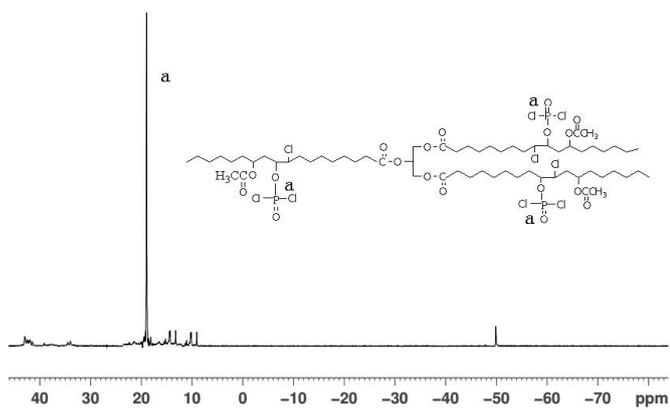


Fig.6 ¹H NMR spectrum of CPECO

and FT-IR spectrum of COPE indicated that esterification reaction of hydroxyl groups of CO with acetic anhydride occurred. The peak at $\delta=5.4$ ppm corresponded to methine group.

In the ¹H NMR spectrum of COPE (Fig.4), the peak (peak 10) at $\delta=5.6$ ppm is corresponding to the double bond protons (-CH=CH-) of fatty acids. In the ¹H NMR spectra of ECOPE, the protons signals in the 5.6 ppm region of the spectrum of ECOPE were disappeared, the multiplets (peak 10) around $\delta=3.1-3.2$ ppm corresponding to protons on the epoxy groups were found in the ¹H NMR spectra of ECOPE (Fig.5). Combining with the FTIR spectrum, we can conclude that epoxidation reaction was occurred completely. In the ¹H NMR spectra of CPECO (Fig.6), the multiplets around $\delta=3.1-3.2$ ppm corresponding to protons on the epoxy groups was disappeared completely comparing with ECOPE, and the region 1.7 ppm (peak 3) is associated with the -P-O-CH- at the middle of the CPECO,²⁵⁻²⁶ which implied that ring opening had occurred following epoxidation with diethyl phosphate.

3.3 ³¹P NMR

Fig.7 ^{31}P NMR spectrum of CPECO

The chemical structure of CPECO was further confirmed by ^{31}P NMR spectra presented in Fig.7. A sharp signal was observed because of the molecular structure containing only one chemical shift of phosphorous atoms. From the above analysis, it is indicated that CPECO has been synthesized successfully.

3.4. LOI tests

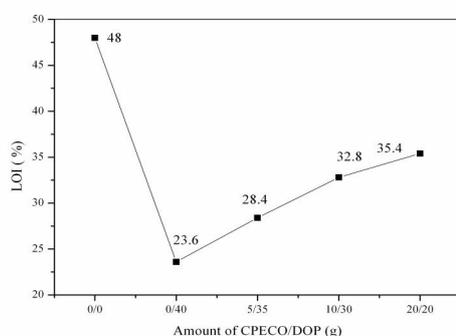


Fig.8 LOI variation in relation to amount of CPECO in PVC blends

The flame retardant properties of PVC blends plasticized with different mass of CPECO were evaluated. The results were presented in Fig.8. PVC is combustible with difficulty because PVC contains large amount of chlorine. After plasticizing with DOP, the LOI value of PVC blends decreased from 48% (PVC0) to 23.6% (PVC1). It demonstrated that DOP was not conducive to flame retardancy of PVC blend. With the increasing content of CPECO in PVC blends, LOI value of PVC4 increased from 23.6% (PVC1) to 35.4% (PVC4). Materials exhibited (LOI) values greater than 26% will show self-extinguishing behaviors and considered to be good flamer retardant.^{13, 27} Therefore, CPECO is effective on flame retardancy for PVC.

3.5. SEM

In order to investigate the carbon forming mechanism further, the microscopic structure of PVC blends after LOI tests was characterized with SEM. Fig. 9 presents the SEM images of the charred layers of PVC blends plasticized with different mass of CPECO. It can be seen from Fig.9 (PVC1) and Fig.9 (PVC2), there are many big holes and crevasses on the surfaces of char residuals. The formation of big holes and crevasses is because many gaschar residuals from the sample PVC3 and PVC4. Just as shown in Fig. 9 (PVC3) and Fig.9 (PVC4), the char layers showed more compact than that of PVC1 and PVC2 and could effectively prevent the transfer heat and oxygen volatilizing into the PVC matrix and increasing the thermal properties. Above of the observations supplied further evidence that CPECO can improve the thermal stability and flame retardancy of PVC blend by improving the quality of carbon and formed a compact and consolidated carburization zone on the surfaces of PVC blends prevented oxygen and heat getting into PVC matrix.

such as HCl and C_6H_6 emitted from surface of PVC matrix in the thermal degradation process. However, with more mass of CPECO mixed with PVC blend, almost no holes and crevasses could be observed from the surfaces of

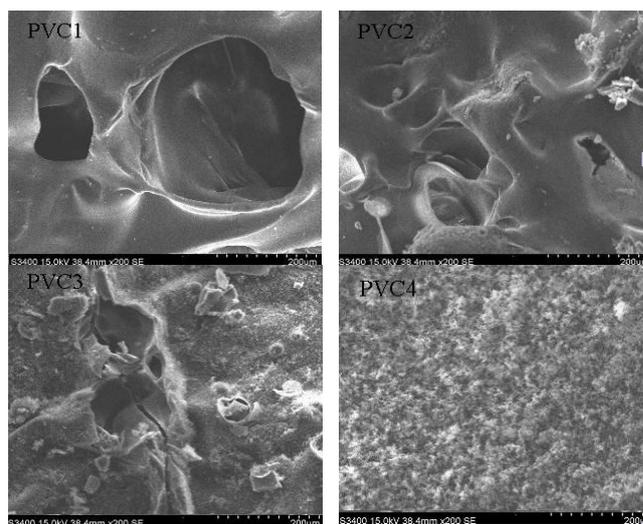


Fig.9 SEM micrographs of surfaces residues after LOI tests

3.6. TGA

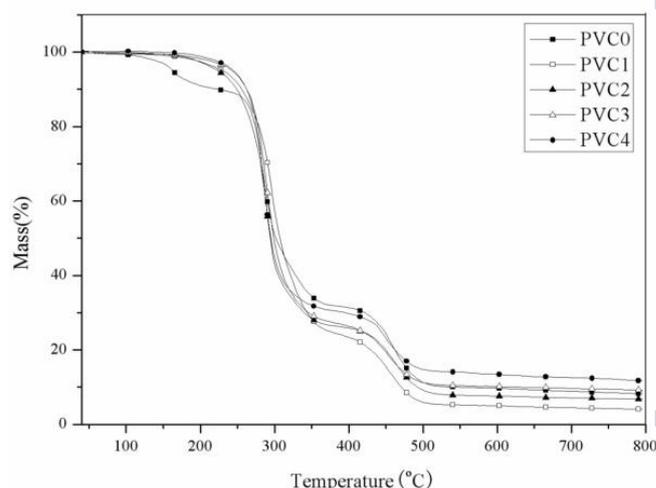


Fig.10 TGA curves of PVC blends

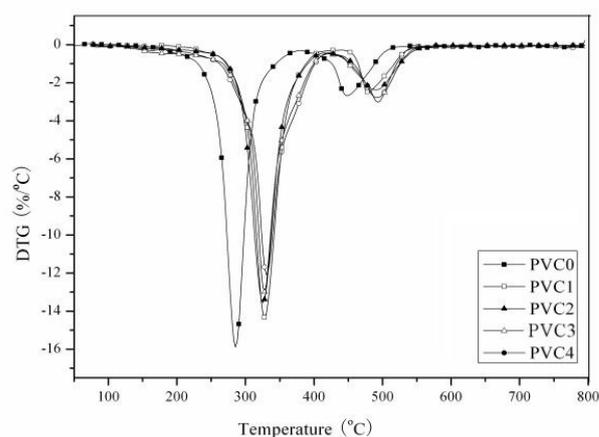


Fig.11 DTG curves of PVC blends

Fig. 10 and Fig. 11 show the TGA and DTG curves of PVC with various contents of CPECO at the linear heating rate of $10\text{ }^\circ\text{C min}^{-1}$, and the corresponding values are given in Table 2. From TGA curves, it can be seen

Table 2 The parameters of TGA of PVC blends

Sample	T_d (°C)	T_{10} (°C)	T_{50} (°C)	T_{P1} (°C)	T_{P2} (°C)	Residual(%)
PVC0	246.3	259.3	279.4	293.8	426.9	9.17
PVC1	256.7	260.7	289.7	210.6	438.9	5.93
PVC2	269.1	266.7	299.6	312.1	436.5	8.29
PVC3	276.3	269.8	306.1	318.6	438.8	14.03
PVC4	280.1	275.0	325.8	322.8	439.4	17.14

that the degradation temperature for PVC0 is 246.3 °C, leaving 6.17% wt. % solid residue at 800°C. When plasticizer cooperated with PVC, degradation temperature increased significantly from 246. °C (PVC0) to 280.1°C. And when DOP was substituted with CPECO, the leaving residue increased gradually from 5.93 wt. % (PVC1) to 17.14% wt. %. Indicating that the two kinds of plasticizers could improve the thermal degradation temperature and CPECO could promote the formation of char residue. There is a two-stage thermal degradation process above 100 °C in the TGA curves of PVC blends. The first stage degradation at around 100 °C-350 °C is the faster stage, which could be corresponded to the formation and stoichiometric elimination of HCl. The second stage at above 350 °C is corresponded to cross linking containing C=C bonds, thermal degradation of polyenes involves cyclization and splitting of chains.^{1, 28} DTG curves of PVC blends showed two degradation peaks at around 310 °C and 440 °C, which are assigned to two faster thermal degradation stages. Table 2 summarized the thermal

properties data of these PVC blends, including decomposition temperature (T_d), 10 % and 50 % weight-loss temperature (T_{10} and T_{50}) and temperature at the maximum weight-loss temperature (T_P). As the increase of mass of CPECO in PVC blends, T_{10} , T_d and T_{P1} increased gradually but T_{P2} almost keep stable at around 438 °C. It can be concluded that CPECO could improve the stability of PVC blends under 440 °C. And the char residual of PVC blends increased

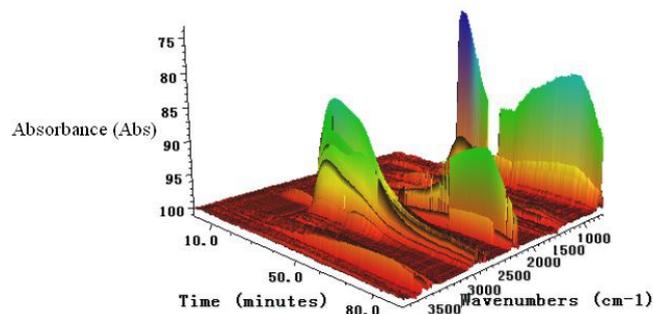


Fig.12 3D FTIR spectra of pyrolysis gas products of PVC0

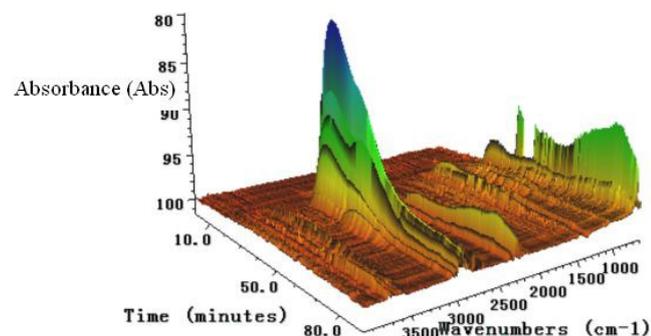


Fig.13 3D FTIR spectra of pyrolysis gas products of PVC1.

from 5.93 % (PVC1) to 17.14 % (PVC4), which indicated that the incorporation of CPECO into PVC blends promoted the formation of char residual.

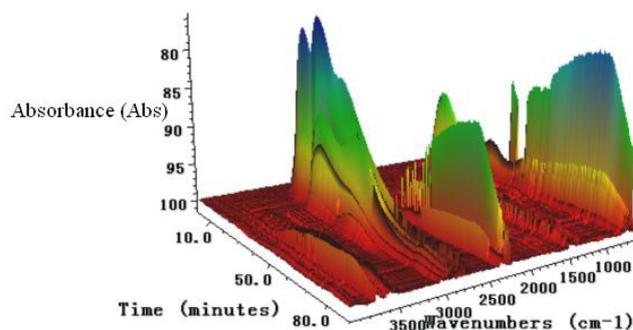


Fig.14 3D FTIR spectra of pyrolysis gas products of PVC4.

3.7. TGA-FTIR

Fig.12, Fig.13 and Fig.14 shows the 3D TGA-FTIR spectrum of gaseous phase in the thermal degradation of PVC0, PVC1 and PVC4, respectively. The main gaseous products of the decomposition of PVC0, PVC1 and PVC4 are similar, which are water (H₂O), carbon dioxide

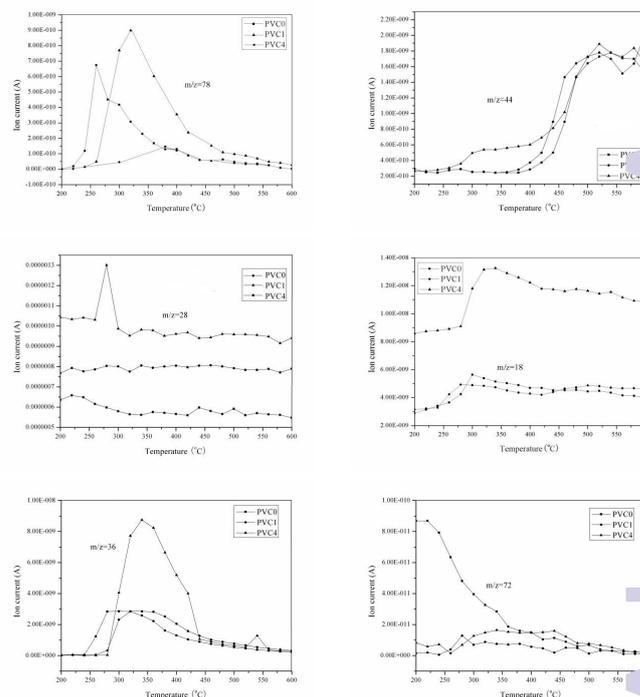


Fig.15 MS signals from the main decomposition products

(CO₂), carbon monoxide (CO), tetrahydrofuran (THF), benzene (C₆H₆) and hydrogen chloride (HCl). Assignment of FTIR absorption bands of the gaseous products was showed in Table 3. At the temperature of fastest decomposition of 320°C, H₂O (3582 cm⁻¹), CO₂ (2372 cm⁻¹), CO (2150 cm⁻¹), THF (2968 cm⁻¹), C₆H₆ (3086 and 1585 cm⁻¹) and HCl (2885.9 cm⁻¹) are all released. Fig. 13 and Fig.14 showed that esters (1743, 1267, and 1103 cm⁻¹) are released. Because DOP and CPECO contained ester groups which

incorporated with the PVC blends. There are many literatures are good agreement with the results.²⁹⁻³² THF is obtained during the thermal degradation products in all of the three samples. Because PVC blends were prepared using THF as the solvent and some THF didn't volatile completely. The number of absorbance bands of PVC0, PVC1 and PVC4 at their maximum weight loss rates is similar to each other for the three samples. PVC blends released large amount of HCl in the thermal degradation process at around 300°C. The results are consistent with TG results. Because from the TG curves of PVC blends, the first stage at around 250 °C- 440 °C is the fastest and corresponded to the formation and stoichiometric elimination of HCl. FTIR of the pyrolysis products of PVC1 blend was similar to that of PVC4 expect for the weak peaks absorbance at 930cm⁻¹, 933 cm⁻¹, and 1639 cm⁻¹ which can be correspond to the P-O-C and P-OH stretching vibration, and the peak absorbance at 2361cm⁻¹ was assigned to P-H.^{29,33} It's because CPECO reacted with PVC mainly in the condensed phase as well as slightly in the gaseous phase during thermal degradation. And most phosphorous-containing components such as P-O-C, P-OH and P-H components were retained in the char residual rather than that in the gaseous phase during thermal degradation. TGA results had been showed that the incorporation of CPECO into PVC blends promoted the formation of char residual, which trapped some of the volatile products and made them participate in the charring reaction. The char layer become a barrier and covered on the PVC matrix which is effective to prohibit the heat flux and air incursion. This surface structure can improve the flame retardancy and thermal stability of PVC blends. To investigate the mechanism of thermal degradation of PVC blends further, TGA-MS was used to conclude the yield of different gases generated during pyrolysis.

3.8. TGA-MS

Because FTIR measurements reveal only qualitative information about the functional group of the different pyrolysis products, MS was performed to explore the exact composition of the pyrolysis products and understand the pyrolysis mechanism in PVC blend plasticized with CPECO. The TGA-MS measurement was heated from 40°C to 800°C under a N₂ atmosphere at a heating of 10 °C / min scanning through m/z in the rang of 2-200. Fig.15 showed the curves for the ion current of different charge-to-mass ratio variation with temperature. Intense ion signals at m/z= 18, 28, 36, 44, 72 and 78 were detected. According the structure of PVC, DOP and CPECO, m/z= 18 is attributed to water. Carbon monoxide is associated with MS signal at m/z=28. The peak at m/z= 36 is attributed to hydrogen chloride. Fragments with m/z=44 and 72 belong to carbon dioxide and tetrahydrofuran, while the peak at m/z= 78 indicates the presence of benzene. The results are consistent

Table 3 Assignment of FTIR absorption bands of the gaseous products

Band position (cm ⁻¹)	Assignment	Reference
4000-3500, 2850-1640, 1560-1400	H ₂ O	29,33,34,40, 42
2360,2370,2372	CO ₂	29, 34,39,40,42
2182	CO	
3055,3080,1585	Benzene	29,35,39
2968	THF	29
930-1030, 1020-1150	P-O-C	34, 35, 37,38,39,41,43
1240-1300,1317	P=O	29,35, 36,37,38,39,40
648,685	Cl ₂	
3422,1639	P-OH	34,36,43
2361	P-H	
1512	Heterpcyclic	
2885	HCl	

with that of TGA-FTIR. Fig. 13 shows the curves for the ion current of

different charge-to-mass ration variation with temperature. For PVC4, the integrated area under carbon monoxide peak at m/z= 28 is smaller than that PVC0 and PVC1, and the integrated area under carbon dioxide peak at m/z=44 is smaller than that of PVC0 and PVC1, indicating that more carbon monoxide and carbon dioxide generated during the degradation process of PVC0 and PVC1, and more carbon residue generated in the degradation process of PVC4. The integrated area under water peak at m/z=18 of PVC4 is larger than that PVC0 and PVC1, meaning that more water is generated during the degradation process. Water could lower the concentration of flammable radicals. The integrated area under benzene peak at m/z=78 of PVC4 is smaller significantly than that PVC0 and PVC1, meaning that more benzene releasing in the degradation process of PVC0 and PVC1, but for PVC4, more carbon residue was produced. From the SEM results, there are many big holes and crevasses on the surfaces of char residuals from the sample PVC1. The formation of big holes and crevasses is because many gas such as carbon monoxide, carbon dioxide, hydrogen chloride and benzene emitted from surface of PVC matrix in the degradation process. In addition more hydrogen chloride emitted in the degradation process of PVC4 than that PVC0 and PVC1 from Fig. 13. The reason may be that part of hydrogen chloride generated form degradation of CPECO. And tetrahydrofuran emitted from all of the PVC blends was similar, because all the PVC blends were prepared using tetrahydrofuran as solvent. Nevertheless, some n-fragments are detected that come from the degradation of PVC4. Intense ion signals at m/z= 32, 47 and 48 were detected. According the structure of PVC and CPECO, fragments with m/z=32, 47 and 48 belong to P-H, P=O and P-OH, respectively. Some researchers reported that metaphosphoric acid and pyrophosphoric acid generated during the thermal degradation of phosphate.^{26,27,29} In this study, liquid metaphosphoric acid and pyrophosphoric acid generated during the thermal degradation of CPECO and formed a protective film on the surface of the carbonaceous char layer. CPECO containing long chain fatty acids supplied a greater abundance of carbon sources in the thermal degradation. It was investigated in the TGA-FTIR that most phosphorous-containing components such as P-O-C, P-OH and P-H components were retained in the char residual rather than in the gaseous phase during thermal degradation. These phosphorous-containing components such as metaphosphoric acid and pyrophosphoric acid and P-O-C, P-OH, P-H

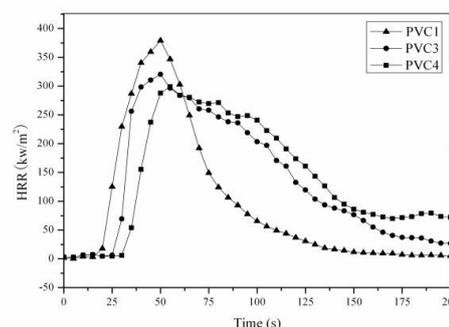


Fig.16 HRR curves of PVC blends.

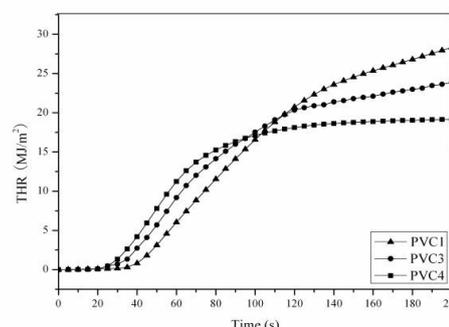


Fig.17 THR curves of PVC blends.

components could promote formation of char residual as dehydrating agent. The char residual was blown by evolving gases which produced a foaming and expansion of the char layer. The carbonaceous char layer is effective

slow mass and heat transfer between the gas and condensed phases and to protect the underlying material from further combustion.

3.9. Cone calorimeter test

The fire behavior of PVC blends was measured with cone calorimeter. The heat release rate (HRR) and total heat release (THR) of PVC blends could be gotten from this test. HRR and THR are regarded as important parameters to evaluate the flame retardant properties of fires. HRR curves and THR curves of PVC1 and PVC4 were showed in Fig. 16 and Fig.17, respectively. From Fig.16, the HRR for PVC1 was characterized by a huge sharp peak heat release (pHRR) of 379.00 kW/m², and there was almost no char residue generated. Indicating PVC plasticized with DOP burnt completely, and DOP improve the flammability of PVC blend. But from HRR curve of PVC3 and PVC4 in Fig. 16, it presented a steady decrease of HRR value after an initial increase to form the char layer. A steady peak heat release (pHRR) of 326 (PVC3) and 289.00 (PVC4) kW/m² could be found in the HRR curve of PVC3 and PVC4. And there is a compact and consolidated carbon residue layer covered on the combustion vessel could be observed. The reason for the decrease of HRR value can be due to the formation of foaming and expansion of the char layer limits the emissions of volatile thermal degradation products and prevents them from oxygen. The carbon residue layer structure could keep the PVC blend thermal stability and improve its flame retardancy. In addition, the THR curves of PVC1 and PVC4 were showed in Fig. 17. It can be found that the THR decreased from 31.78 MJ/m² (PVC1) to 19.12 MJ/m² (PVC4). It indicated that CPECO could reduce the flammability of PVC blend and improve the flame retardant properties of PVC blends to substitute for DOP as a secondary plasticizer.

3.10 DMA

The lower glass transition temperature (T_g) of PVC blends indicating that the compatibility of PVC and the plasticizer is more excellent.⁴⁴ The dynamic mechanical property of PVC blends was measured by DMA and the DMA curves of PVC blends were showed in Fig 18. It can be seen that all of the plasticized PVC blends showed only a $\tan \delta$ peak, indicating that CPECO was compatible with PVC. T_g of PVC1, PVC2, PVC3 and PVC4 is 41.2, 51.4, 54.3 and 58.6 °C, respectively. With the amount of CPECO increasing in the PVC blends, T_g values increased from 41.2 °C (PVC1) to 58.6 °C (PVC4), implying that compatibility of PVC with DOP was better than that of CPECO.

3.11 Mechanical property

Mechanical properties PVC blends are important index to evaluate the plasticizing effect of plasticizer. All of the samples were characterized with universal tensile testing machine. The obtained tensile strength, elongation at break and modulus of elasticity were showed in Table 4. When PVC cooperated with plasticizer such as DOP and CPECO, the tensile strength decreased and the elongation at break increased compared with that neat PVC (PVC0). It means that DOP and CPECO have a plasticizing effect on PVC. With DOP substituted by CPECO in PVC blends, the tensile strength increased from 20.08 Mpa (PVC1) to 25.05 Mpa (PVC4). And the elongation at break decreased from 505.35% (PVC1) to 467.32 % (PVC4),

Table 4 The mechanical properties of PVC blends

Sample	Tensile strength (Mpa)	Elongation at break (%)	Modulus of elasticity (Mpa)
PVC0	26.60	167.21	197.11
PVC1	20.08	505.35	18.93
PVC2	21.32	485.34	32.57
PVC3	23.15	468.5	35.39
PVC4	25.05	467.32	43.77

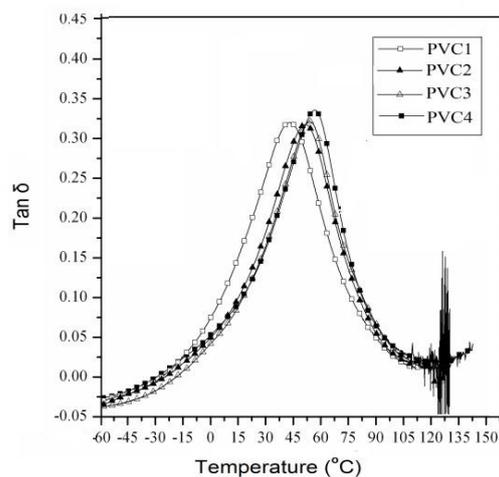


Fig.18 DMA curves of PVC blends.

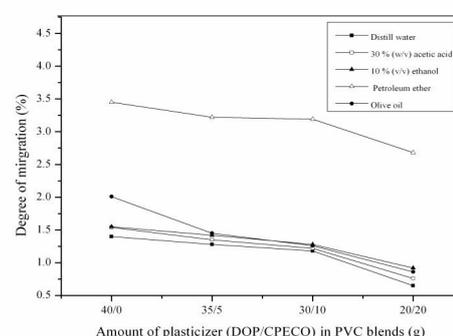


Fig.19 Degree of migration of plasticizer

The results indicated that CPECO had plasticizing effect on PVC.

3.12 Migration stability tests

Migration stability is an important property of plasticizer. The loss of plasticizer could cause changes in the long-time properties of the PVC products as well as possible toxic and biological effect when the plasticizers are transferred to human. The migration stability of CPECO in PVC blends was investigated by the leaching tests using five different solvents and the results were presented in Fig.19. Every value was the average of the values for five specimens. It is impressive to observe that with DOP substituted by CPECO in PVC blends, the loss mass of plasticizer become less gradually in all five different solvents. It indicated that the migration resistance of CPECO was better than that of DOP. The high migration resistance of CPECO could keep property of PVC products long-term stabilization.

4. Conclusions

A novel flame retardant plasticizer CPECO was synthesized from castor oil. The chemical structure of CPECO was characterized with FTIR, ¹H NMR and ³¹P NMR. Effect of CPECO on thermal degradation of PVC blends and its flame retardant mechanism as secondary plasticizer was studied. When 50 % wt of DOP substituted with CPECO in PVC blends, LOI value of PVC blends could increase from 23.6% to 35.4%. TGA showed that CPECO could improve the stability of PVC blends under 440 °C. TGA-FTIR and TGA-MS detected that the main pyrolysis products of PVC blends were H₂O, HCl, CO₂, CO and C₆H₆.

Liquid metaphosphoric acid and pyrophosphoric acid generated during the thermal degradation of CPECO and formed a protective film on the surface of the carbonaceous char layer. Long chain fatty acids were contained in the structure of CPECO which supplied a greater abundance of carbon sources in the thermal degradation. TGA-FTIR and TGA-MS illustrated that most phosphorous-containing components such as P-O-C, P-OH and P-H components were retained in the char residual rather than that in the gaseous phase during thermal degradation. These phosphorous-containing

components such as metaphosphoric acid and pyrophosphoric acid and P-O-C, P-OH, P-H components could promote formation of char residual as dehydrating agent. The char residual was blown by evolving gases which produced a foaming and expansion of the char layer. The carbonaceous char layer is effective to slow mass and heat transfer between the gas and condensed phases and to protect the underlying material from further combustion. And a small quantity of phosphorous-containing components emitted in the gaseous phase during thermal degradation could dilute and isolate oxygen to slow burning.

The T_g and mechanical properties of PVC blends plasticized with CPECO is closed to that of the PVC blends only plasticized with DOP. More important, CPECO plasticized PVC blends exhibits lower migration in distill water, olive oil, 10 % (v/v) ethanol, 30 % (w/v) acetic acid and petroleum ether than that of DOP. The high migration resistance of CPECO could keep property of PVC products long-term stabilization. In view of the excellent thermal stability, flame retardancy, mechanical properties and lower migration of PVC blend plasticized with CPECO as secondary plasticizer. We are sure that CPECO can satisfy the demand of plasticization and can help researchers to design and explore novel flame retardant plasticizer and apply them in harsh conditions.

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Notes and references

- M. A. D. Silva, M. G. A. Vieira, A. C. G. Maçumoto and M.M. Beppu, *Polym. Test.*, 2011, **30**, 478-784.
- Y. Saeki and T. Emura, *Prog. Polym. Sci.*, 2002, **27**, 2055-2131.
- P. Jiang and Y. Zhou, *Environmentally friendly plasticizer*, National defense industry press, 2nd edn, Beijing, 2008, pp. 2-3.
- J. A. Tickner, T. Schettler, T. Guidotti, M. McCally and M. Rossi, *Am. J. Ind. Med.*, 2001, **39**, 100-111.
- D. K. Agarwal, W. H. Lawrence, J. E. Turner and J. Autian, *J. Toxicol. Environ. Health*, 1989, **26**, 71-84.
- S. Oishi, *Arch. Toxicol.*, 1990, **64**, 143-147.
- H. A. Dirven, P. H. Broek and F. Jongeneelen, *J. Toxicol (Amsterdam)*, 1990, **65**, 199-207.
- K. A. Treinen and J. Heindel, *J. Reprod Toxicol.*, 1992, **6**, 143-148.
- P. Grasso, J. J. Heindel, C. J. Powell and L. E. Reichert, *Biol. Reprod.*, 1993, **48**, 454-459.
- Y. I. Kicheva, V. D. Kostov and M. Chichovska, *Biomaterials*, 1995, **16**, 575-579.
- S. V. Levchik and E. D. Weil, *Polym. Adv. Technol.*, 2005, **16**, 707-716.
- A. Marklund, B. Andersson and P. Haglund, *J. Environ. Monit.*, 2005, **7**, 814-819.
- L. Ying-Ling, C. Yie-Chan and C. Tsung-Yu, *Polym. Int.*, 2003, **52**, 1256-1261.
- J. Li, C. H. Ke, L. Xu and Y. Z. Wang, *Polym. Degrad. Stab.*, 2012, **97**, 1107-1113.
- P. Yang, J. Yan, H. Sun, H. Fan, Y. Chen, F. Wang and B. Shi, *RSC Adv.*, 2013, **11**, 1-3.
- N. Lardjane, N. Belhaneche-Bensemra and V. Massardier, *J. Polym. Res.*, 2013, **20**, 209-219.
- T. Sun and R. Thom, *J. Elastom. Plast.*, 2010, **42**, 129-137.
- O. Y. S. Palacios, P. C. R. Narvaez, C. C. Jean-Pierre, M. C. Pardo and C. Fonteix, *J. Vin. Add. Tech.*, 2014, **20**, 65-71.
- M. M. Sander, A. Nicolau, R. Guzzato and D. Samios, *Polym. Test.*, 2012; **31**:1077-1082.
- C. Bueno-Ferrer, M. C. Garrigós and A. Jiménez, *Polym. Degrad. Stab.*, 2012, **95**, 2207-2212.
- P. Karmalm, T. Hjertberg, A. Jansson and R. Dahl, *Polym. Degrad. Stab.*, 2009, **94**, 2275-2281.
- Y. Ou, X. Ding and L. Zhang, *J. Appl. Polym. Sci.* 014, DOI: 10.1002/APP.39763
- K. Padmasiri, Gamage, S. Ahmed and Farid, *J. Appl. Polym. Sci.*, 2011, **121**, 823-838.
- B. Yang, Y. Bai and Y. Cao, *J. Appl. Polym. Sci.*, 2010, **115**, 2178-2182.
- L. Q. Zhang, M. Zhang, L. H. Hu and Y. H. Zhou, *Polymer. Degrad. Stab.* 2014, **98**, 2784-2794.
- L. Q. Zhang, M. Zhang, L. H. Hu and Y. H. Zhou, *Ind. Crop. Prod.*, 2014, **52**, 380-388.
- L. L. Pan, G. Y. Li, Y. C. Su and J. S. Lian, *Polym. Degrad. Stab.* 2012, **97**, 1801-1806.
- J. Li, C. H. Ke, L. Xu and Y. Z. Wang, *Polym. Degrad. Stab.*, 2012, **97**, 1107-1113.
- Q. Hongqiang, L. Xin, X. Jianzhong, Haiyun M, Yunhong J and Jixing X *Ind. Eng. Chem. Res.*, 2014, **53**, 8476-8483
- S. V. Levchik and E. D. A. Weil, *Polym. Adv. Technol.*, 2004, **15**, 691-670.
- G. Botelho, A. Queiro's, A. Liberal and S. Gijsman, *Polym. Degrad. Stab.*, 2001, **74**, 39-48.
- A. Balabanovich, T. Zevaco and W. Schnabel, *Macromol. Mater. Eng.*, 2004, **289**, 181-190.
- A. Balabanovich, *Ta*, 2005, **435**, 188-196.
- J. Weizhong, Jianwei and H. Zhidong, *Polym. Degrad. Stab.*, 2012, **97**, 632-637.
- C. Jun, L. Shumei and Z. Jianqing, *Polym. Degrad. Stab.*, 2011, **96**, 1508-1515.
- P. Hua-qiao, Z. Qian, W. De-yi, C. Li and W. Yuzhong, *Ind. Eng. Chem. Res.*, 2008, **14**, 589-595.
- Z. Jing, S. Lei, N. Shibin and H. Yuan, *Polym. Degrad. Stab.*, 2009, **94**, 291-296.
- W. Deyi, C. Xiaoxia, Q. Minghai, L. Yun, W. Junsheng and W. Yuzhong *Polym. Degrad. Stab.*, 2008, **93**, 2186-2192.
- S. Shiqiang, M. Jiajun, C. Ke, C. Guanjuan, H. Yawen and Y. Junxiao *Polym. Degrad. Stab.*, 2014, **99**, 43-52.
- Q. Lijun, Y. Longjian, Q. Yong and Q. Shuren., *Polymer*. 2011, **52**, 5486-5493.
- S. Zhou, L. Song, Z. Z. Wang, Y. Hu and W. Y. Xing, *Polym. Degrad. Stab.*, 2008, **93**, 1799-1806.
- Z. Z. Wang, P. Lv and K. L. Hu, *J. Anal. Appl. Pyrol.*, 2009, **86**, 207-214.
- K. Wu, L. Song, H. D. Hu, B. K. Kandol and E. Kandare, *Prog. Org. Coat.* 2009, **65**, 490-497.
- Y. Li, C. Wang, G. Wang and Z. Qu, *J. Wuhan Univ. Technol.*, 2008, **2** 101-104.