

Synthesis of a novel phosphorus-containing plasticizer based on castor oil and its application for flame retardancy of polyvinyl chloride

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Abstract—A novel flame-retardant plasticizer based on castor oil (FRC) was synthesized, and its potential application for polyvinyl chloride (PVC) was evaluated through the study of torque during melt processing, thermogravimetric analysis (TGA), limiting oxygen index instrument, scanning electron microscope (SEM) and mechanical tests. The results suggested that the FRC has a plasticizing effect in blends with PVC. The addition of FRC resulted in reduction of processing torque, good compatibility, improvement in thermal stability and efficient flame retardant. Torque reduction was observed (33.6%), indicating the reduction of viscosity and the improvement of process. The increase (31.9%) of LOI value indicated that incorporation of FRC system had obviously improved the flame retardant property of PVC blends. The excellent flame retardant properties were obtained by forming an isolation layer on the surface of PVC blends in the process of FRC burning. FRC could improve the thermal ability of PVC blends by enhancing the decomposition temperature of PVC. The performance in all properties of PVC products could be obtained by controlling the formula blends. Therefore, castor oil-based flame retardant plasticizers would appear suitable for a wide range of application.

Keywords: Plasticizer, Castor Oil, Flame-retardant, PVC

INTRODUCTION

Phthalates as the main plasticizer additives of PVC have been used for years because of excellent plasticizing effect; the effect is mainly to improve the flexibility and thermal stability by lowering the second-order transition temperature, and to reduce the tension of deformation, hardness, viscosity and electrostatic charge of PVC. However, phthalates may migrate from PVC products to environments when the materials contact with biological fluids, which will take potential risks to human health when is used in food packing, automotive products, insect repellents, blood storage bags and medical devices [1-4]. The use of phthalate esters has been strongly restricted in childcare products and packing of foods and drugs [5,6]. The raw materials of phthalate esters are mainly petrochemicals and dependent on oil resources. So developing a new plasticizer without toxicity from renewable resources is a pressing mission as oil prices get higher.

A series of recent publications have reported the synthesis and possible application of PVC plasticizers derived from renewable resources. Silva et al. [7] prepared a natural polymeric plasticizer through polyesterification of rice fatty acid. Wu [8] synthesized a biobased aliphatic polyester from 1, 4-butanediol and 2-methylsuccinate acid via direct and polycondensation route. The plas-

ticizer had superior migration resistance property to the low-molecular weight plasticizer DOP for PVC. Riaz, Martini and Fenollar et al. [9-11] prepared epoxidized linseed oil and evaluated the plasticized effect to PVC. The thermal stability of PVC plasticized with epoxidized soybean oil was characterized by Bueno-Ferrer et al. [12]. Castor is a renewable resource that has potential uses as an environment-friendly plasticizer for medical and commodity plastics. Mehta et al. [13,14] prepared a bio-based plasticizer by two-step esterification reaction of castor oil fatty acid with benzyl and octanoic acid. Gamage et al. [15] investigated the plasticizing and stabilizing effects of epoxidized Madhuca (Mee) oil and its derivatives on PVC. Sunflower can be epoxidized and the epoxidized sunflower oil has potential use a plasticizer for PVC. Benaniba and Lardjane et al. [16,17] studied the synthesis and characterization of epoxidized sunflower oil; they found that the di-(2-ethyl hexyl) phthalate could be replaced by epoxidized sunflower oil as bio-based plasticizer for flexible PVC. The other bio-based plasticizers such as low-molecular-weight glycerol ester, epoxidized safflower oil and oleic acid polyester were studied [18-20].

Vegetable oil as a good plasticizer has been used in products with high value-added widely because of non-toxic, biodegrade, renewable and environmental protection. The present study synthesized a novel phosphorus-containing plasticizer based on castor oil (FRC) and evaluated the performance of FRC in PVC for the first time. The functional plasticizer was combined with renewable resources of castor oil and flame retardant functional group. As far as we know, phosphorus-containing plasticizer based on cas-

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tor oil has not been reported in any literature.

EXPERIMENTAL

1. Material and Chemical

Castor oil (industrial grade) was purchased from Sinopharm Chemical Reagent. Glycerol, hydrogen peroxide, phosphoric acid

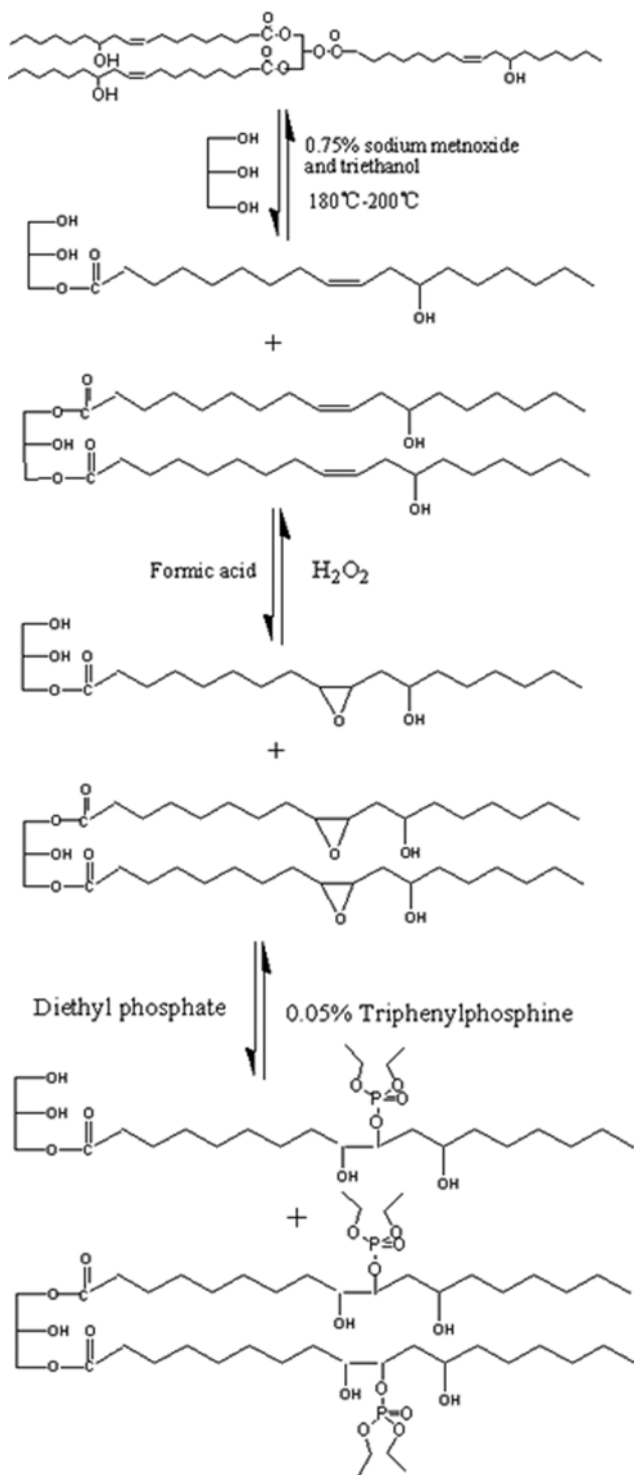


Fig. 1. The synthesis process of FRC.

and triethylamine were provided by Nanjing Chemical Reagent Co. Ltd. Triphenylphosphine and sodium methoxide were from Shanghai Zhanyun Co. Ltd.

2. Method

2-1. Synthesis of Castor Oil-based Flame Retardant Plasticizer

FRC was synthesized through a three-step procedure of alcoholysis, epoxidation and ring opening reaction. First, glycerol was heated at 180 °C–220 °C for 2 h under N_2 atmosphere before glycerolysis to remove trace amounts of water. The reaction was carried out using the molal ratio of 1 mol castor oil and 2 mol glycerol. The castor oil was added in five steps at 1 h intervals. The sodium methoxide and triethanolamine (0.75% wt) were also added as catalyst; the solution was heated 3 h at 180 °C–220 °C. Then the reaction flask was cooled by immersion in an ice and salt mixture to room temperature, the product was washed three times with distilled water, and the initial excess of glycerol was removed. The alcoholysis reaction is shown in Fig. 1. The aim of the second step is to prepare the epoxidized glycerolysis castor oil. The epoxidation reaction is shown in Fig. 1. The glycerolysis castor oil (200 g), formic acid (14.5 g) and phosphoric acid (0.5 g) were put into a three-necked round-bottom flask equipped with a tetrafluoroethylene stirrer, a thermometer and a condenser pipe. After heating to 40 °C in oil bath, hydrogen peroxide was dropped into the reaction flask in 30 min. The mixture was heated to 70 °C and stirred for 4 h. Then the reaction mixture was cooled to room temperature and washed to pH=7 with sodium hydroxide solution, then the product was dried over anhydrous sodium sulfate. The last step was to prepare flame-retarded plasticizer based castor oil (FRC). 100 g epoxidized glycerolysis castor oil and 75 g toluene were mixed in a three-necked round-bottom flask equipped with a tetrafluoroethylene stirrer, a thermometer and a condenser pipe. The mixture of diethyl phosphate (30 g), toluene (75 g) and triphenylphosphine (0.5 g) was dropped in the reaction in 30 min at 40 °C. The reaction proceeded with continuous stirring at 75 °C for 4 h. Then the reaction mixture was cooled to room temperature and washed to pH=7 with sodium hydroxide solution and washed three times with distilled water; then the water was removed with rotary evaporator at 60 °C. The chemical reaction process of FRC is shown in Fig. 1 [21,22].

2-2. Preparation of Blends

The PVC was pre-treated by drying at 60 °C for 2 h to eliminate possible absorbed water on the surface of particle. Dumbbell-shaped samples of blends were molded on a MiniJetII Micro-injection molding machine (Hakke Instrument Crop., Germany) according GB/T 17037.1-1997 (China). Moulding conditions were set at 165 °C for 5 min at 550 bar.

3. Material Characterization

3-1. Evaluation of Torque

Blends were melt processed at 165 °C for 5 min at 50 rpm using a Poly Lab Torque rheometer (Hakke Instrument Crop., Germany). The formulations used for preparing plasticized PVC blends are shown in Table 1.

3-2. TGA

TGA was performed in a TG209F1 TGA thermal analysis instrument (Netzsch Instrument Crop., Germany) in N_2 atmosphere (50 ml/min) at a heating rate of 10 °C/min. The samples were put into

Table 1. Formulations used for preparing plasticized PVC blends

Samples	PVC (g)	DOP (g)	FRC (g)	Calcium carbonate (g)	Thermal stabilizers (g)	Calcined clay (g)
PVC0	50	20	0	5	1	5
PVC5	50	15	5	5	1	5
PVC10	50	10	10	5	1	5
PVC15	50	5	15	5	1	5
PVC20	50	0	20	5	1	5

platinum pans and scanned from ambient temperature to 600 °C.

3-3. Flame Retardant Properties

The combustion test was according to the standard of plastics-determination of burning behavior by oxygen index (GB/T 2406.1-2008, China) using JF-3 oxygen index measuring instrument (Nanjing Lei Instrument Co. Ltd., China), and UL-94 test using CFZ-3 type vertical burning test instrument (Desheng Testing Instrument Co. Ltd., China). The size (4×10×80 mm) of samples was prepared according ASTM D2863. UL-94 test results are classified by burning rating V-0, V-1, V-2, and V-0 denotes the best flame retardant.

3-4. Mechanical Properties

Tensile modulus, tensile strength, and elongation at break were determined according 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 at least.

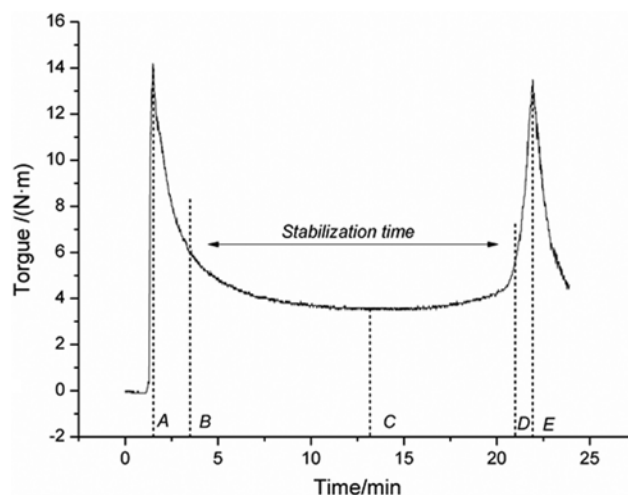
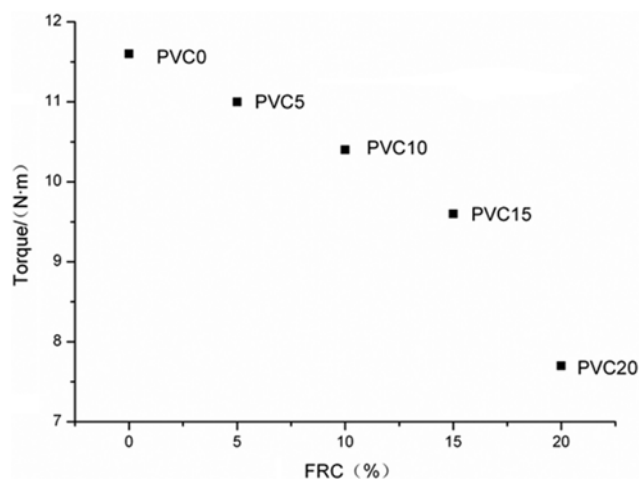
3-5. SEM

A Hitachi 3400-1 (Hitachi, Japan) scanning electron microscope instrument, operated at 12kv, was used to observe the surface of PVC blends and residual char of PVC blends. The surface of PVC blends was sputtered with gold after molding on a MiniJetII Micro-injection molding machine for SEM observation. The residual char of PVC blends was sputtered with gold after LOI tests for SEM observation.

RESULTS AND DISCUSSION

1. Evaluation of Torque

To verify the melting behavior, processing data were collected during mixing in the Haake chamber. The three important variables in this process are chamber temperature, rotating speed and rotor torque. The chamber temperature and rotating speed were fixed, and the torque data were collected and related directly to the melt viscosity, the material resistance to flow. During processing, the melt temperature remained approximately constant. The normal torque rheological curve of PVC blends and the figure of torque values relative to the proportion of FRC in the blends are shown in Fig. 2 and Fig. 3. Seen from the Fig. 2, point A is the feeding peak which indicates the maximum torque; the points B, C, D and E are stable torque, minimum torque, starting point of degradation and end of degradation, respectively. PVC material should be taken from torque rheometer and the plasticizing processing should be stopped at the point of stable torque. PVC will start degrading after a time. Fig. 3 presents the torque values relative to the proportion of FRC in PVC blends for the processing time of 5 min.

**Fig. 2. Torque rheological curve of PVC.****Fig. 3. Torque variation during blends mixing in relation to the FRC content.**

From Fig. 3, with the increasing of FRC, the torque of PVC blends decreased from 11.6 N·m (PVC0) to 7.7 N·m (PVC20), which corresponds to 33.6% reduction. The torque reduction is the first cri-

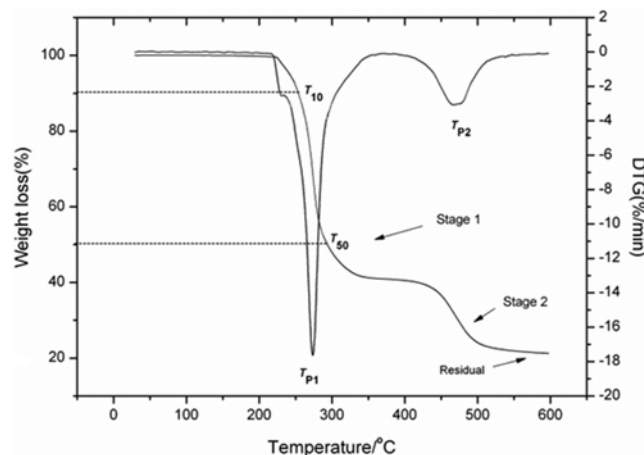
**Fig. 4. TGA curves of PVC blend samples.**

Table 2. Thermal properties data of PVC blends

Sample	T_d (°C)	T_{10} (°C)	T_{50} (°C)	T_{p1} (°C)	T_{p2} (°C)	Residual (%)
PVC0	249.4	258.1	283.2	278.9	457.3	17.02%
PVC5	252.3	259.3	283.9	279.5	458.6	16.19%
PVC10	260.8	261.7	284.1	288.4	457.5	15.74%
PVC15	262.9	265.2	284.1	292.3	458.2	15.32%
PVC20	268.7	268.3	284.0	299.0	457.9	14.71%

terion that indicates that the FRC acts as a plasticizer, reducing the viscosity of the melt and improving the processing.

2. TGA

The thermal stability of PVC blends was evaluated by means of TGA. The TGA curves and thermal properties of PVC blends are shown in Fig. 4 and Table 2. All of the PVC blends exhibited a two-stage thermal degradation process above 250 °C. The first stage degradation at about 250 °C–470 °C is mainly corresponding to information and stoichiometric elimination of HCl. The second stage at about (>470 °C) corresponds to gradual degradation of the char residue. Table 2 summarizes the thermal properties data of these PVC blends, including 10% and 50% weight-loss temperature (T_{10} and T_{50}) and temperature at the maximum weight-loss temperature rate (T_p). TGA curves of PVC blends without FRC showed two degradation peaks at around 278.9 °C and 457.3 °C. The first plateau relates to the dehydrochlorination of PVC, with information and stoichiometric elimination of HCl, while the second is attributed to polymer cross linked containing C=C bonds. Thermal degradation of PVC involves cyclization and splitting of chains [24, 25]. TGA curves of PVC blends and PVC blends plasticized with FRC showed similar behavior with two mass loss peaks. With the increase of content of FRC, T_{10} , degradation temperature (T_g) and T_{p1} increased, while T_{50} and T_{p2} were almost unchanged. The increase of T_{10} , degradation temperature (T_d) and T_{p1} is mainly attributed to the decomposition of DOP plasticizer, which indicates that the decomposition of DOP mainly happened at below 280 °C and the thermal stability of DOP is inferior to FRC.

With the addition of FRC, the residual of PVC blends decreased from 17.02% to 14.71; the residual is attributed to the inert filler such as calcium carbonate. So the thermal stability of FRC is superior to DOP, which could enhance the decomposition temperature of PVC.

3. Flame Retardant Properties

To evaluate flame retardant properties of PVC blends, LOI and UL-94 test were conducted and the relative data presented in Table 3. PVC blend without FRC has an LOI value of 24.1%; with the addition of FRC, the LOI value increased from 24.1% to 31.8%, which corresponds to 31.9% addition. It indicates that FRC is effective in prompting flame retardance. Generally, materials exhibiting LOI values greater than 26 will show self-extinguishing behavior and are considered to be good flame retardant [26]. Hence, the increase of LOI value indicates that incorporation of FRC system has obviously improved the flame retardant properties of PVC blends (Table 3). The sample PVC0 only achieves the V-1 ranking in UL-94 test and burns with flammable dripping, after blending with FRC, the samples achieve the V-0 ranking in UL-94 test and burns with-

Table 3. The detailed data obtained from LOI and UL-94 measurement

Samples	Thickness/mm	Width (mm)	Length (mm)	LOI (%)	Ranking
PVC0	4	10	80	24.1	V-1
PVC5	4	10	80	26.4	V-0
PVC10	4	10	80	28.4	V-0
PVC15	4	10	80	29.6	V-0
PVC20	4	10	80	31.8	V-0

Table 4. The detail mechanical properties of PVC blends

Samples	Tensile strength (Mpa)	Elongation at break (%)	Modulus of elasticity (Mpa)
PVC0	16.32	350.12	6.8
PVC5	12.01	282.53	18.24
PVC10	10.67	235.19	86.8
PVC15	8.74	170.8	105.65
PVC20	6.21	135.7	117.04

out flammable dripping, the results signify that FRC is an effective flame retardant material.

4. Mechanical Properties

The mechanical properties of PVC blends depend on the resin and additives used in their composition: the plasticizer and material itself. Hence, the tensile strength along with elongation at break is a good effective way to evaluate the efficiency of plasticizers. The values of the mechanical properties of PVC blends are presented in Table 4. A significant influence of the addition of different content FRC for PVC blends could be observed. With the addition of FRC and reduction of DOP in the PVC blends, it caused a significant decrease of 61.94% in tensile strength and approximately 60% in elongation at break. All of the mechanical properties illustrate that the FRC has plasticization in PVC, but the plasticizing efficiency is lower than DOP. The results indicate that FRC molecular has less electron atmosphere than DOP molecular, and the interaction between FRC molecular and PVC molecular is weaker than the interaction between DOP molecular and PVC molecular. However, we can get appropriate PVC products by modifying formula of PVC blends.

5. SEM

Scanning electron microscopy was used to observe surface morphology of PVC blends. Many particles and gaps can be observed on the external surface of PVC0 in Fig. 5(a); the particles and gaps appearing on the surface indicate that some plasticizer and fillers are scattered outside the PVC matrix. PVC blends added with FRC presented few particles and gaps. SEM micrographs of PVC surface revealed a smoother surface with the addition of FRC than PVC without it from the surface of PVC5, PVC10, PVC15 and PVC20, which is shown in Fig. 5(b), Fig. 5(c), Fig. 5(d) and Fig. 5(e), respectively. It indicates that FRC could disperse in the PVC matrix uniformly and surrounded intimately with PVC continuous phase, and there is not a clear boundary between them. So there is good compatibility between FRC and PVC. This phenomenon could be

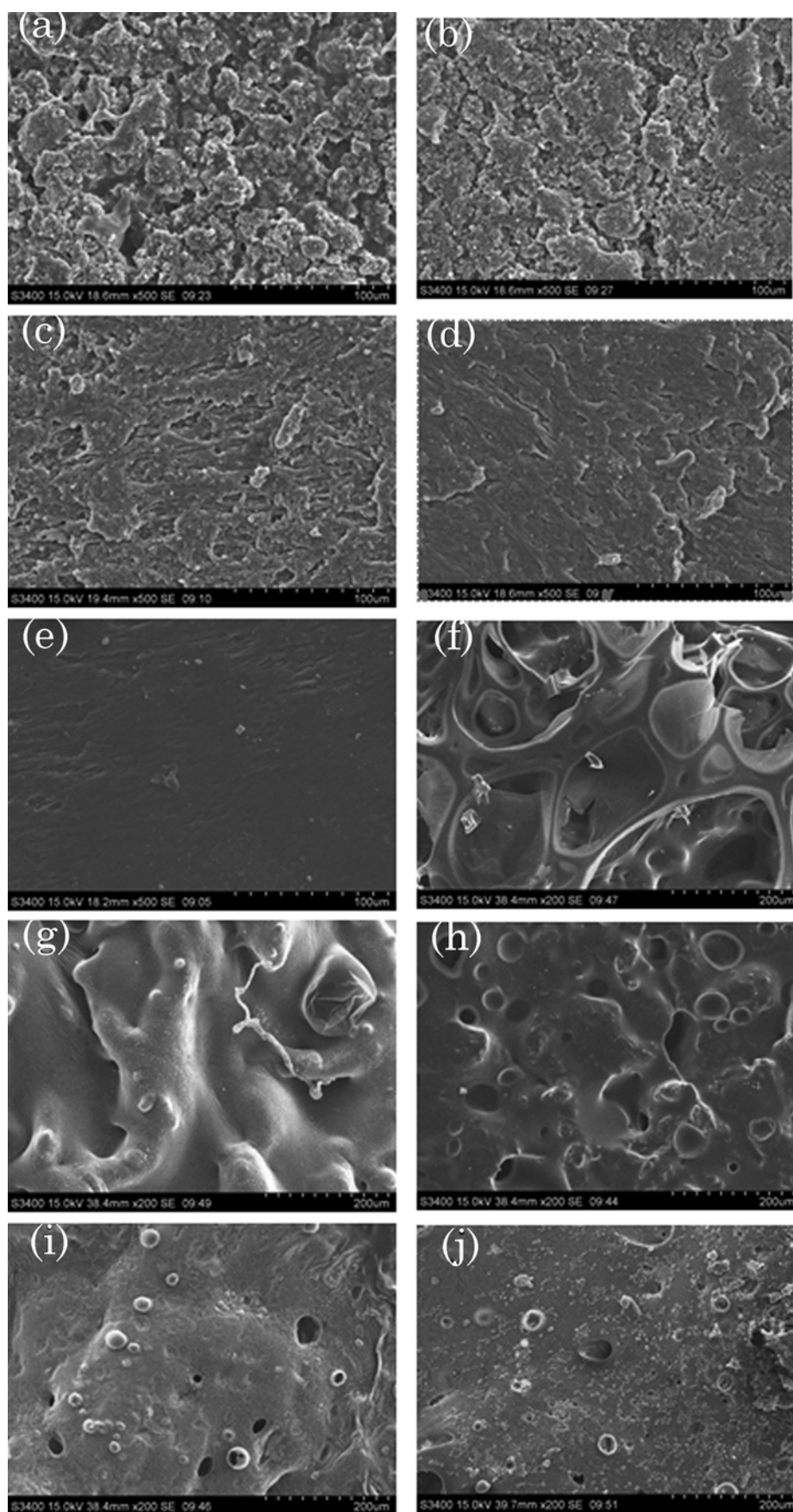


Fig. 5. SEM micrographs of surfaces of PVC blends (a), (b), (c), (d), (e) and PVC blends residues (f), (g), (h), (I), (j).

explained as that the interaction between oxygen atom in the FRC and hydrogen atom in the PVC could improve the incorporation of FRC and various fillers into the PVC matrix.

Fig. 5(f), (g), (h), (I), (j) shows the SEM images of the residual char after limit oxygen index test. Surface morphology of residual char is different compared to each other with the increase of FRC. From Fig. 5(f), the char surface of PVC0 is separated by a net of cracks; the width of cracks is about 200 μm , and a large number of irregular micro bubble structures distributed on the surface of char residue. The incomplete char coat cannot effectively prohibit heat flux and air incursion penetrating the underlying heat polymer. The physical structure of the charring layer plays an important role in the performance of the flame retardancy. Therefore, DOP could not play any role in the performance of the flame retardant. On the contrary, the char surfaces of PVC15 and PVC20 are continuous and compact, which is shown in Fig. 5(i) and Fig. 5(j), and any crack could not be observed, indicating that the carbonization layer between the FRC and the PVC matrix was compact. P-O and P-C bonds existing in the structure of FRC makes it still thermally stable under 350 °C. The existence of diethyl phosphate grafting in the castor oil phosphate molecular chain, diethyl phosphate degraded and phosphinic acid was generated when it was burned. Metaphosphate and poly metaphosphate would be generated after dehydration of phosphinic acid. They could promote polymer carbonization and form a consolidated and thick flame retardant coating quickly. From Fig. 5(i) and Fig. 5(j), it can be seen that the char layer of the flame retardant coating is consolidated and thick, which effectively prohibits the degradation products penetrating the underlying heated polymer. The flame retardant coating plays an important role in the performance of the flame retardant.

CONCLUSIONS

A new flame-retarded plasticizer based castor oil (FRC) was synthesized by a three-step procedure of alcoholysis, epoxidation and ring opening reaction of castor oil, glycerin, formic acid and diethyl phosphate. The potential application of FRC as a plasticizer of PVC was characterized with torque during melt processing, FT IR, TGA, oxygen index, SEM and mechanical tests. Torque reduction (33.6%) indicated the reduction of viscosity and the improvement of the process. The increase of LOI value indicates that incorporation of FRC system has obviously improved the flame retardant properties of PVC blends. The excellent flame retardant properties were obtained by forming an isolation layer on the surface of PVC blends in the process of FRC burning. FRC could improve the thermal ability of PVC blends by enhancing the decomposition temperature of PVC. The performance in all property of PVC products could be obtained by controlling the formula blends. The incorporation of the FRC in PVC matrix showed promising results, indicating potential application that will be further investigated.

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