

폴리염화비닐의 친환경 가소제로서 Poly(1,2-propylene glycol adipate)

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Poly(1,2-propylene glycol adipate) as an Environmentally Friendly Plasticizer for Poly(vinyl chloride)

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Abstract: Poly(1,2-propylene glycol adipate) (PPA) was used as an environmentally friendly plasticizer in flexible poly(vinyl chloride) (PVC). Thermal, mechanical, and rheological properties of the PVC/PPA blends were characterized by differential scanning calorimetry, dynamic mechanical analysis, tensile test, scanning electron microscopy and small amplitude oscillatory shear rheometry. The results showed that PPA lowered the glass transition temperature of PVC. The introduction of PPA could decrease tensile strength and Young's modulus of the PVC/PPA blends; however, elongation-at-break was dramatically increased due to the plastic deformation. The plasticization effect of PPA was also manifested by the decrease of dynamic storage modulus and viscosity in the melt state of the blends. The results indicated that PPA had a good plasticizing effect on PVC.

Keywords: poly(vinyl chloride), poly(1,2-propylene glycol adipate), plasticizer, blends, mechanical properties.

Introduction

Poly(vinyl chloride) (PVC) is the third most consumed polymeric material worldwide, with wide applications in areas including construction, tubing, medical devices and electronics packaging.¹ Due to the brittle nature of the neat PVC, it is often compounded with plasticizers to enhance its flexibility and toughness for various applications, and the most commonly used plasticizers for PVC are phthalate esters.² They constitute 97% of the total amount of plasticizers are usually added in concentrations up to 50% of the final weight of the products.³ Phthalate esters are low molecular weight compounds that are

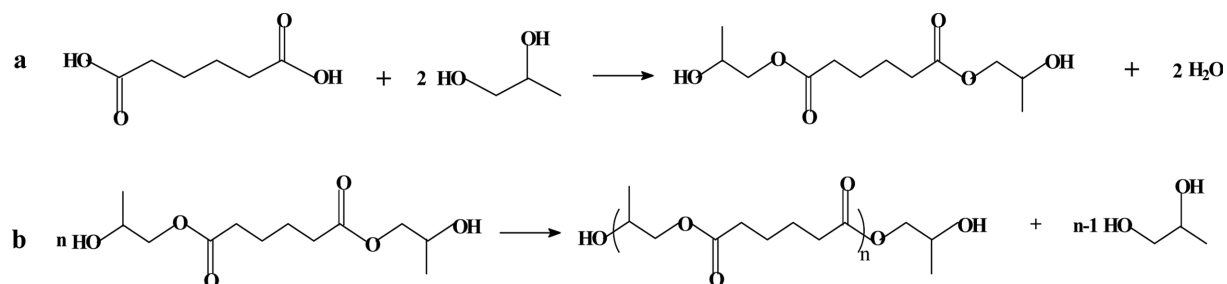
easily released from the polymer matrix. They have been found in most environments, in domestic foods and wastes, in animals and humans. When used in applications such as medical devices or toys, the contact with biological fluids or synthetic substitutes causes transfer of plasticizer to humans.⁴⁻⁹

In December 1999, the European Commission issued an emergency ban on the use of six phthalate esters (diisononyl phthalate, diisodecyl phthalate, bis(2-ethylhexyl) phthalate (DEHP or DOP), dibutyl phthalate, benzyl butyl phthalate, and dioctyl phthalate) in toys and childcare articles. Following the European ban, also other countries including USA and Canada have introduced regulations regarding the use of these phthalate esters in toys and childcare articles.⁴ Many studies have been conducted to seek for several alternative plasticizers that have been suggested to replace phthalate esters used in

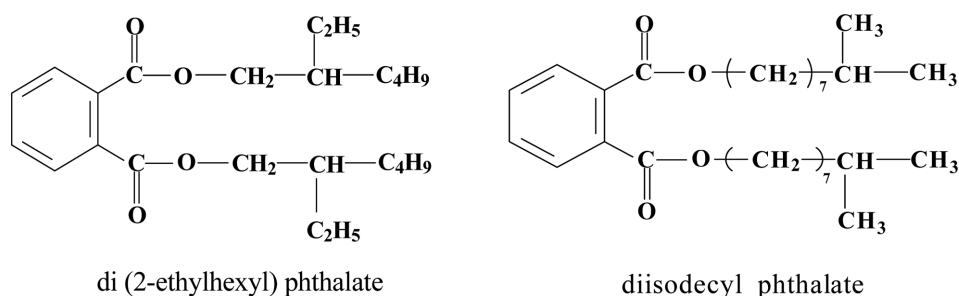
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Scheme 1. Synthesis of poly(1,2-propylene glycol adipate).



Scheme 2. Structures of traditional plasticizers.

PVC.^{1,10,11}

The polyester plasticizers in this research are a kind of additives for PVC with good characteristics. They have the excellent performances of low toxicity, low volatility, and solvents withstanding. The polyester plasticizers are called the “permanent plasticizers” and are now being studied as replacements for traditional plasticizers.^{12,13} Using adipic acid, 1,2-propylene glycol, as raw materials, poly(1,2-propylene glycol adipate) (PPA) was prepared via polyesterification reaction (Scheme 1). Comparing to structures of traditional plasticizers (Scheme 2), PPA is nontoxic and biodegradable polymer. The use of environmentally benign plasticizers is a way to improve the health and environmental issues concerning plasticizers.¹⁴ In this article, the study is mainly focused on the miscibility, thermal, dynamic mechanical properties, mechanical properties, and rheological behavior of PVC/PPA blends.

Experimental

Materials. PVC resin (trade name SG-5, k-value 68~66, 1135~981) was supplied by Siping Haohua Chemical Co., Ltd., China. Dibutyltin dilaurate was obtained from Tianjin Chemical Industry Co., Ltd., China. Poly(1,2-propylene glycol adipate) (PPA) was synthesized via polyesterification reaction using 1,2-propylene glycol and adipic acid as raw materials by our laboratory.¹² In addition, tetra-*n*-butyl titanate and isoc-

tanol were used as a catalyst and chain-ending reagent for the reaction, respectively. They were purchased from the Sinopharm Chemical Reagent Co., Ltd. PPA has weight-average molecular weight (M_w) of 8.30×10^3 g/mol and the polydispersity index of 1.57.

Preparation of PVC/PPA. PVC resin was dried at 80 °C for 4 h in a vacuum oven before usage. PVC resin and required amounts of additives were shown in Table 1. The PVC/PPA blends were prepared by using a high-speed mixer (GH-100DY) from room temperature to 100 °C. The mixing compositions of the PVC/PPA blends were 100/0, 100/20, 100/40, 100/60, and 100/80 w/w. The PVC samples used in pure PVC and all blends contained 3 phr dibutyltin dilaurate in order to minimize degradation. To guarantee the PPA well distributed in the PVC matrix, the mixing process was repeated several times. All of the samples were sealed and retained 24 h. The

Table 1. Components of PVC Samples

PVC/PPA (w/w)	Material component (phr)		
	PVC	Dibutyltin dilaurate	PPA
100/0	100	3	0
100/20	100	3	20
100/40	100	3	40
100/60	100	3	60
100/80	100	3	80

samples obtained were further melt blended using a single screw extruder at a rotating speed 40 rpm at 170–185 °C to mix granulation. Then, all of the samples were compression-molded into sheets with thicknesses of 1.0 mm at 180 °C for various tests.

Characterization

Migration of PPA. For migration measurement, all reagents were in chromatographic grade. PPA used as a standard solution was prepared in dehydrated ethanol. 1.000 g of samples were introduced into volumetric flasks (10 mL) and extracted at room temperature with dehydrated ethanol with shaking.

The experiments of PPA extraction from the solvent were determined at room temperature using a high performance liquid chromatography (HPLC) system equipped with a constant flow-rate pump LC 10-AS (Shimadzu, Kyoto, Japan), a manual injection valve, and a constant-wavelength ultraviolet light detector SPD 10-AVP (Shimadzu, Kyoto, Japan), all of which were connected to a data integrator C-R8A (Shimadzu, Kyoto, Japan). A column ACCHROM® XAqua C₁₈ (250×4.6 mm, 5.0 μm) were used. The mobile phase was a mixture of methanol-water (80:20, v/v). The flow rate was 1.0 mL/min and the injection volume was 10 μL. The detection wavelength was set at 220 nm. The migration rate of the samples was calculated using the formula:

$$\text{Migration rate (\%)} = \frac{W_1}{W_2} \times 100 \quad (1)$$

where W_1 is the weight of the extracted PPA tested by HPLC; W_2 , initial weight of the test specimen.

Differential Scanning Calorimetry. The thermal properties of the blends were investigated by a TA Instruments differential scanning calorimeter DSC Q20 (USA) under N₂ atmosphere. The specimens were crimp sealed in aluminum crucibles and had a nominal weight of about 6 mg. Samples were heated from -60 to 100 °C at a rate of 10 °C/min under a nitrogen gas flow of 50 mL/min. Pure PVC and pure PPA were heated to 100 °C also in the same heating rate.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) was carried out with a DMA/SDTA861[®] apparatus (Mettler-Toledo, Switzerland) in the tensile mode, which provided the plots of the storage modules (E') and the mechanical loss ($\tan\delta$) against temperature. The samples were sized $W \times H \times L = 4 \times 1 \times 9 \text{ mm}^3$. All tests were conducted at a frequency of 1 Hz and a heating rate of 3 °C/min as a function of tem-

perature from -80 to 100 °C.

Thermal Stability. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 PC simultaneous thermal analysis instrument. All samples with weight of 10±0.2 mg were heated from room temperature to 600 °C at 10 K/min under nitrogen.

Tensile Properties. Uniaxial tensile tests were carried out on dumbbell shaped specimens ($W \times H \times L = 4 \times 1 \times 20 \text{ mm}^3$) which were punched out from the compression-molded sheets. The measurements were performed using a tensile-testing machine (Instron-1121, Canton, MA) according to ASTM D638-2008 at a crosshead speed of 50 mm/min. All tests were carried out at room temperature and 50% relative humidity. At least five specimens were tested for each sample to get an average value.

Shore A Hardness. The shore A hardness test was carried out according to ISO 7619 using a Zwick 7206 hardness tester. This method is based on an indenter penetration test and requires a sample thickness. Three measurements were made on each sample type.

Morphological Characterization. The cryogenically fractured surfaces of 100/60 and 100/80 PVC/PPA blends were characterized by scanning electron microscopy (SEM) (model Japan JXA-840 ESEMFE), respectively. A layer of gold was sputter-coated uniformly over all of the fractured surfaces before SEM observations.

Rheological Properties. Melt flow indices (MFIs) of the pure PVC and PVC/PPA blends were determined with a μ PXRZ-400B melt flow indexer (Changchun, China) equipped with a standard die. The die had a smooth straight bore with a diameter of 2.0955±0.005 mm and a length of 8.000±0.025 mm. The measurements were performed according to ASTM D1238-82. The conducted temperature was 190 °C.

Rheological measurements of the blends were carried out on a Physica MCR 2000 rheometer (AR 2000ex). Frequency sweep for the PVC/PPA samples was carried out under nitrogen using 25 mm plate-plate geometry. The gap distance between the parallel plates was 0.9 mm for all tests. The sheet samples were about 1.0 mm in thickness. A strain sweep test was initially conducted to determine the linear viscoelastic region of the materials. The angular frequency range used during testing was 0.1–100 rad/s. The temperatures were plotted at 180 °C.

Results and Discussion

Migration of PPA. PVC plasticizers can be released from

flexible PVC in different ways: (1) volatilization from the PVC surface to the air, (2) extraction from PVC to a liquid in contact with it, (3) migration from PVC to a solid or semisolid in contact with it, (4) exudation under pressure.^{15,16}

It was found that PPA was easily soluble in dehydrated ethanol through test. Dehydrated ethanol was used as the extraction medium in the evaluation of PPA extraction. It had been

used to evaluate the migration stability of polyester plasticizers in plasticized PVC samples. A series of typical HPLC chromatograms of PPA solution were shown in Figure 1.

The PPA migration rates of PVC/PPA samples containing different amount of PPA were shown in Figure 2. With the addition of PPA, the migration rate of the PVC/PPA blends increased from 0.113% to 0.180%. PPA exhibited the lower migration rate in PVC matrix.

Comparing to conventional plasticizer such as DOP,¹³ the migration rate of 100/30 PVC/DOP blend was 7%, and the migration rate of 100/50 PVC/DOP blend was 22%. DOP indicated higher migration rate and poor resistance to migration in PVC matrix. Comparing with DOP, PPA was a good with-standing migration PVC plasticizer.

Thermal Properties. The DSC heating thermograms of the PVC/PPA blends were shown in Figure 3. The T_g of neat PPA was -44.8°C . The T_g decreased from 86.1°C of neat PVC to -14.2°C of PVC/PPA 100/80 blend with the increase of PPA content in the blends, it manifested that the increase of PPA content in the blends enhanced the plasticity of PVC/PPA blends. It also can be seen that there was only one peak for each curve in the DSC heating thermograms. This indicates that PPA is miscible with PVC.

Fox equation was used to further discuss the PVC/PPA system. The Fox equation¹⁷ was as follows:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (2)$$

where W_i is weight fraction of pure component i , T_g is the blend and T_{gi} is the glasstemperature of pure component i . Fig-

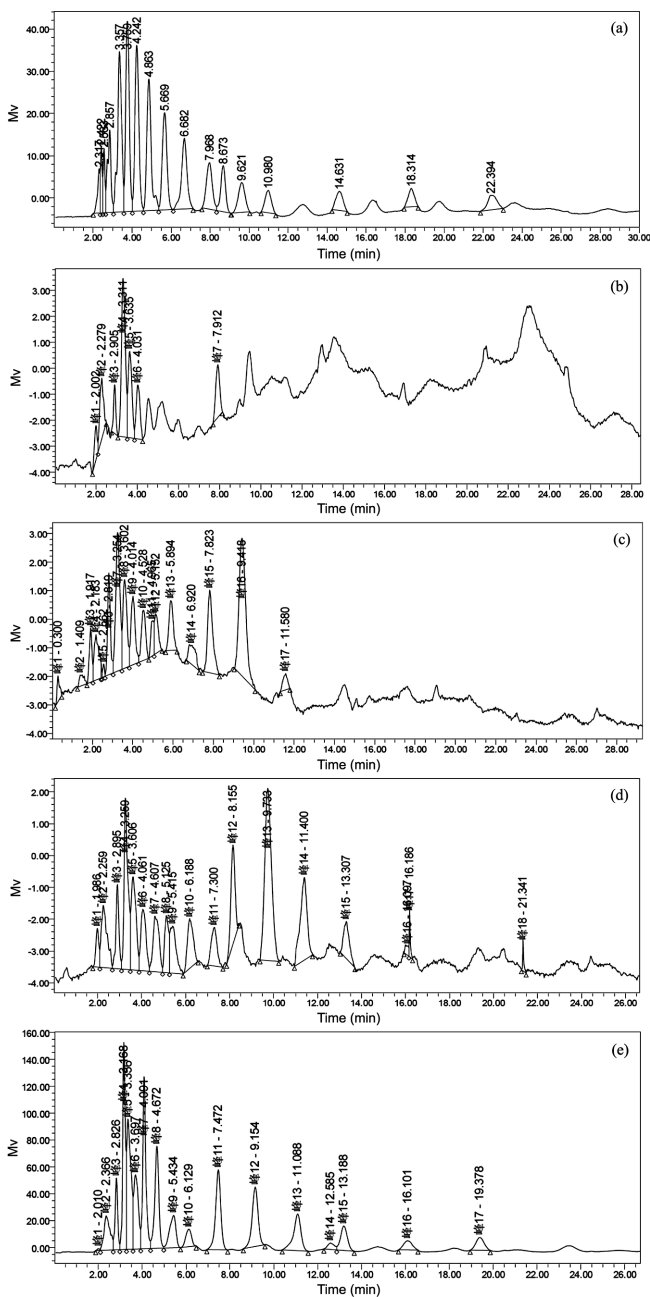


Figure 1. A series of typical HPLC chromatograms of PPA solutions: (a) standard solution of PPA; (b) 100/20; (c) 100/40; (d) 100/60; (e) 100/80 PVC/PPA blends.

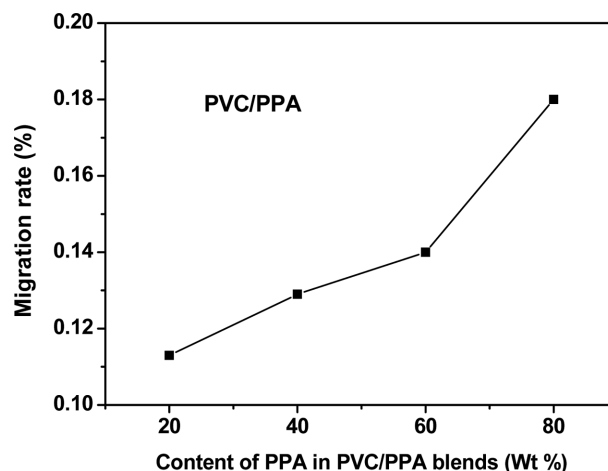


Figure 2. Migration rate plotted against PPA content for PVC/PPA blends.

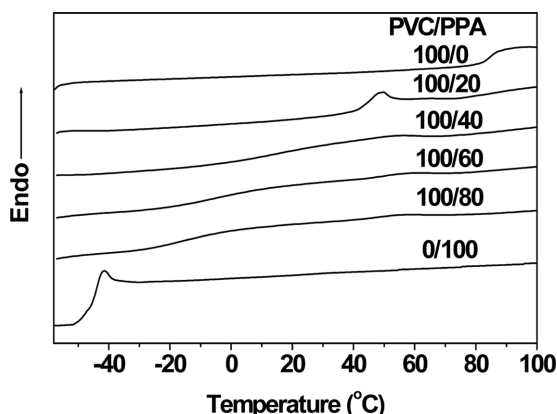


Figure 3. DSC thermograms of PVC, PPA and PVC/PPA blends.

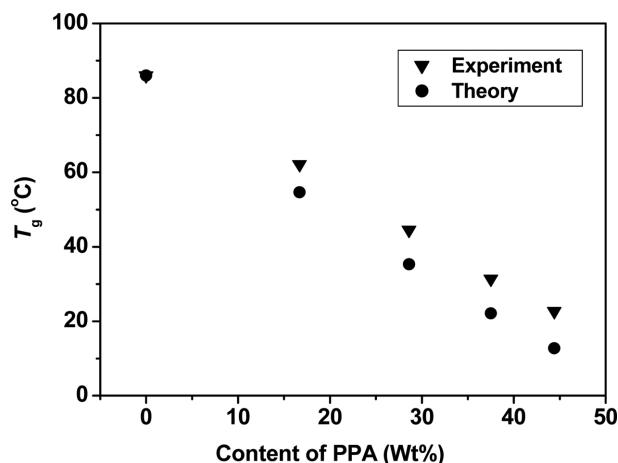


Figure 4. Glass transition temperatures as a function of PPA weight fraction.

Figure 4 showed that when the variation of T_g fitted the Fox equation, and the result indicated that the PPA was miscible with PVC at selective content.

DMA experiments were carried out to further test the miscibility of PVC/PPA blends. Variations of dynamic storage modulus (E') of the samples with temperature are shown in Figure 5(a). It can be seen that the storage modulus of the PVC/PPA blends decreased with the increase of PPA content in the blends. The increase of PPA content in the blends decreased the rigidity of PVC/PPA blends around $-60 \sim -20^\circ\text{C}$. Moreover, there was a large drop of the storage modulus around $-20 \sim 60^\circ\text{C}$ corresponding to the glass transition region of the PVC/PPA blends, it manifested the plasticity of PVC/PPA blends enhanced.

Figure 5(b) displayed the dynamic loss curves versus the temperature of neat PVC and the PVC/PPA blends. The glass transition temperatures could also be determined by the peak

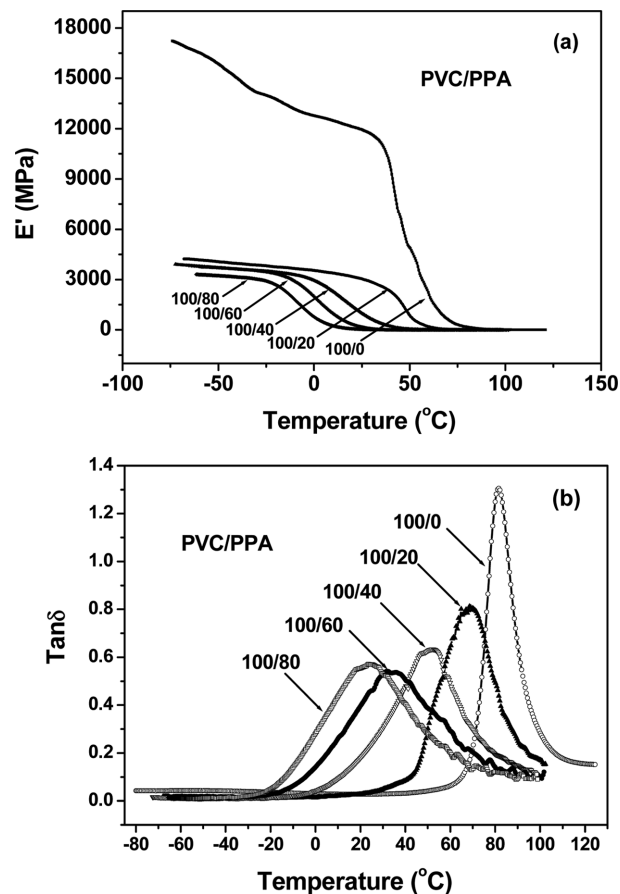


Figure 5. Dynamic mechanical properties of PVC/PPA blends: (a) the storage modulus; (b) $\tan\delta$.

Table 2. Glass Transition Parameters of PVC/PPA Blends

PVC/PPA (w/w)	PVC/PPA	
	Width of transition in DSC ($^\circ\text{C}$)	FWHM in DMA ($^\circ\text{C}$)
100/0	10.4	9.67
100/20	14.6	31.8
100/40	28.1	40.7
100/60	33.7	47.5
100/80	37.2	50.8

temperature from the dynamic loss ($\tan\delta$) curves. The plasticization of PPA led to glass transition temperature of PVC/PPA blends shifting to lower temperature. It can be seen that PVC/PPA blends exhibited a single glass transition peak, suggesting that PVC was miscible with PPA, which is consistent with the DSC analysis. The full width-at-half-maximum (FWHM) was calculated by $\tan\delta$. The parameters of width were listed in Table 2. The transitional width of PVC increased from 10.4 to 37.2 $^\circ\text{C}$ in DSC, the FWHM of PVC increased

from 9.67 to 50.8 °C in DMA. It indicated that the plasticity of PVC was enhanced due to the addition of PPA. Likewise, the Hildebrand solubility parameter was used to further discuss the PVC/PPA system. The Hildebrand solubility parameter equation¹⁸ was as follows:

$$\delta = (E_{\text{coh}}/V)^{1/2} \quad (3)$$

where δ is solubility parameter, E_{coh} is the cohesive energy density and V is the per unit molar volume. From the eq. (3), the solubility parameter of PPA was 18.3. That the solubility parameter of PVC has been reported by A. Agrawal *et al.*¹⁶ was 19.4. The results indicated that PVC was partially miscible with PPA, it was consistent with the results of DSC.

Thermal Stability. The TGA and DTG curves of the samples are shown in Figure 6 and correlative values of decomposed temperature for the samples are listed in Table 3.

From the TGA curves, the composites revealed two-stage degradation: the first stage attributes to the volatilization of

Table 3. Characters Temperatures of TGA and DTG Curves

PVC/PPA(w/w)	T_{onset} (°C)	T_{max}^1 (°C)	T_{max}^2 (°C)
100/0	231.03	268.84	446.28
100/20	234.45	269.61	446.70
100/40	238.23	270.06	447.03
100//60	241.20	270.13	446.21
100/80	253.17	275.28	450.50
0/100	274.01	385.89	-

hydrogen chloride molecules followed by the formation of the conjugated polyene sequences, while the second stage corresponds to the thermal cracking of the carbonaceous conjugated polyene sequences.¹⁹⁻²² The temperature corresponding to the onset of decomposition (T_{onset} , at weight loss of 10 wt%) for a polymer was essential for evaluating its thermal stability and guiding melt processing. According to the TGA analysis, it could be observed that the T_{onset} increased with increasing PPA content. The T_{onset} increased from 231.03 °C for the pure PVC to 253.17 °C for the 100/80 PVC/PPA blend. This indicated that PPA had the positive effect on the thermal stability of PVC.

Another important thermal characteristic parameter for a polymer is the temperature corresponding to the maximum rate of weight loss (T_{max}), which is defined as the peak value of the first derivative TGA curve as a function of temperature. The first derivative curves for pure PVC, pure PPA, and PVC/PPA blends are shown in Figure 6(b) and their T_{max} values are listed in Table 1. T_{max}^1 and T_{max}^2 were denoted as the thermal decomposition temperature with the max rate of the volatilization of hydrogen chloride molecules and the fracture of macromolecular chain, respectively. It could be clearly seen that PVC/PPA blends had shown slightly higher T_{max} than that of pure PVC. In addition, the rate of weight loss for pure PVC was greater than that of pure PPA, which indicated that the stability property of PVC was worse than that of PPA. Therefore, the addition of PPA could improve the thermal stability properties of PVC/PPA blends.

Tensile Properties. The addition of PPA significantly changed the tensile behavior from brittle fracture to ductile fracture. The stress-strain curves of pure PVC and PVC/PPA blends are shown in Figure 7. The mechanical properties of PVC/PPA blends are given in Table 4. It can be seen that all of the PVC/PPA blends exhibited a ductile behavior with yielding and a subsequent plastic deformation. Neat PVC exhibited an elongation at break value of 93%. The elongation

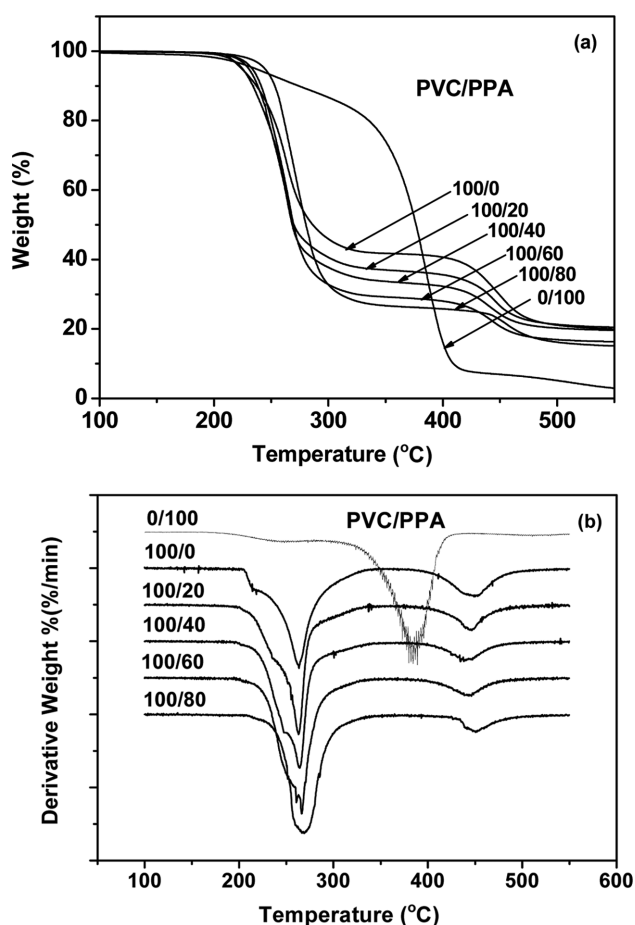


Figure 6. TGA and DTG curves of pure PVC and PVC/PPA blends.

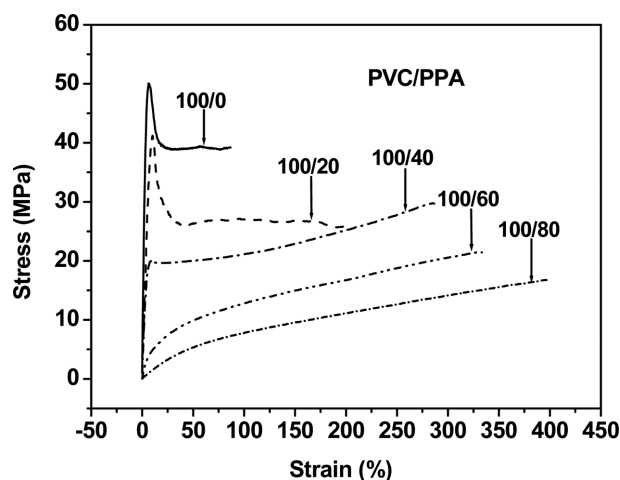


Figure 7. Tensile behavior of PVC/PPA blends.

at break of the PVC/PPA blends increased with the addition of PPA. The highest elongation at break was increased to 399% for the 100/80 PVC/PPA blend. Such a neat increase in elongation at break is believed to be the increase of molecular chain mobility resulting from the decrease of T_g . The yield stress, for example, decreased from 50.0 MPa for neat PVC to 29.8 MPa for the 100/40 PVC/PPA blend. The increase of PPA content to 100/80 PVC/PPA blend further decreased the yield stress to about 16.8 MPa.

Measuring the slope of Young's modulus curve is the common method of determining the stiffness. From Table 4, the 100/0 PVC/PPA exhibits a modulus value of 1470 MPa, and the addition of PPA significantly decreases the stiffness. It was evident that the increase of PPA from 0 to 80 phr leads to the decrease of the modulus value from 1470 to 15 MPa. Table 4 also shows that Shore A hardness decreased from 96 to 78 with the addition of PPA, such reduction in hardness is attributed to the plasticizing effect of the PPA. As discussed in above, the increased flexibility of the PVC/PPA blends was accompanied with a decrease in tensile strength, yield stress, Young's modulus and Shore A hardness. The effect of plas-

Table 4. Mechanical Properties of PVC/PPA Blends

PVC/PPA (w/w)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Shore A hardness
100/0	1470±34	50.0±2.2	93±3	96±0.3
100/20	597±43	41.3±3.1	210±12	90±0.1
100/40	462±35	29.8±2.7	286.2±24	84±0.1
100/60	82±36	21.5±2.2	333.8±35	80±0.2
100/80	15±17	16.8±1.6	399.0±43	78±0.5

ticizers is usually to decrease the T_g of PVC and improve the ductility and softness of PVC. PPA is miscible with the PVC acting as a plasticizer.

Morphology. The SEM images of the cryogenically fracture surfaces of pure PVC and PVC/PPA blends are shown in Figure 8. From Figure 8(a)-(e), single plasticizer phases could nearly be detected in the PVC/PPA blends. SEM of PVC/PPA blends micrographs show very good compatible morphologies without the edge, cavity, and holes resulting from poor interfacial adhesion. All of the PVC/PPA blends exhibit a uniform phase, indicating that PPA is evenly distributed in the PVC matrix.

Rheological Properties. The MFIs of neat PVC and the PVC/PPA blends were determined, and the results were shown in Figure 9.

Figure 9 demonstrated the effect of mass percentage of the samples on MFI. With the addition of PPA, the MFI of PVC/PPA blends had a sharp increase. Although the neat PVC had

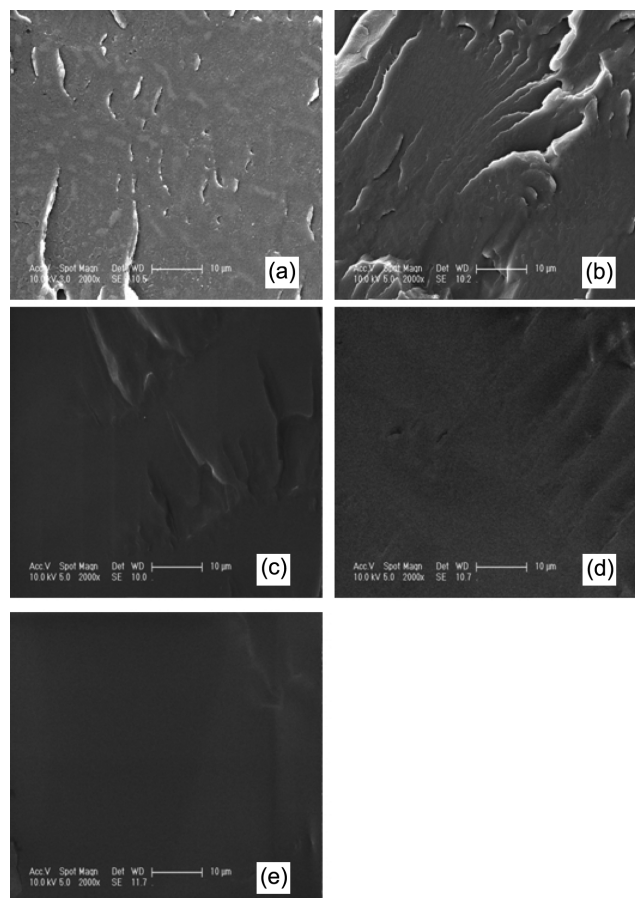


Figure 8. SEM micrographs of the cryogenically fractured surfaces of PVC/PPA blends: (a) 100/0; (b) 100/20; (c) 100/40; (d) 100/60; (e) 100/80.

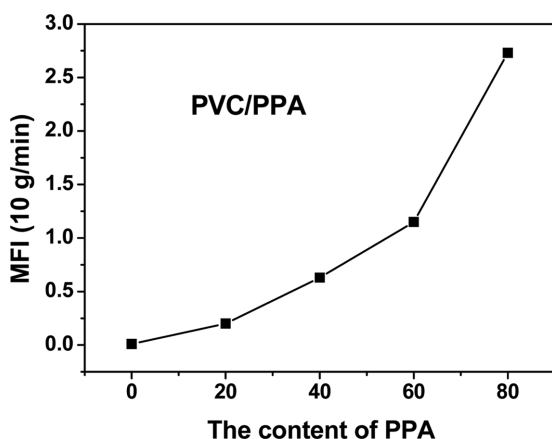


Figure 9. Variations of MFI for PVC and PVC/PPA blends.

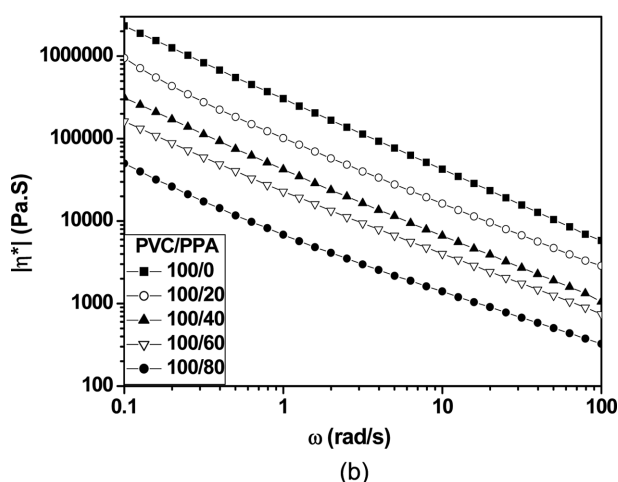
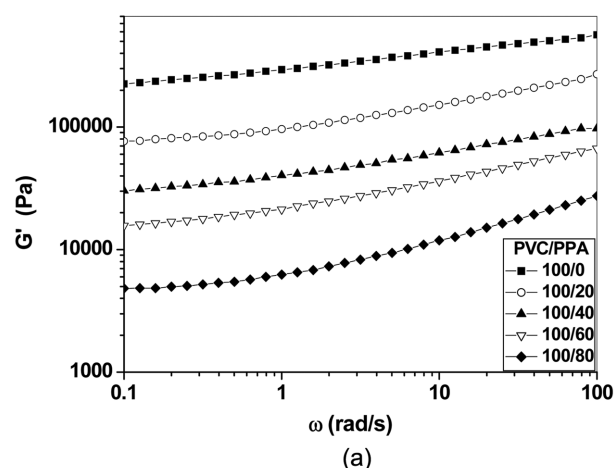


Figure 10. Frequency dependence of (a) dynamic storage modulus; (b) complex viscosity of PVC/PPA blends.

the MFI of 0.01 g/10 min, the MFI increase to 2.73 g/10 min for the 100/80 PVC/PPA blend. The experimental results indicated that the melt flow ability of PVC was increased with the

addition of PPA. The increased MFI exhibited that the system of the melt flow resistance was reduced and the melt viscosity was decreased. Therefore, PPA was a good plasticizer for PVC.

The dynamic rheological experiments were carried out for the PVC/PPA blends with the whole compositions. Figure 10(a) displayed the relationship between storage modulus and angular frequency of the PVC/PPA blends. It could be seen that the G' of PVC/PPA blends decreased with the increase of PPA content in the blends. The lower storage modulus of the blends is supposed to be originated from the decrease in brittleness of the blends.

Figure 10(b) displayed the relationship between complex viscosity and angular frequency of the PVC/PPA blends. It exhibits that the melt viscosity of the blends are substantially lower with the addition of PPA. For example, at 10 rad/s, the melt viscosity of the 100/80 PVC/PPA blend was reduced by about 3.4% compared to that of the 100/0 PVC/PPA blend. It also can be seen that the PVC/PPA blends showed non-Newtonian behavior at whole frequency region. The decreased melt viscosity of the blend can be related to an increased free volume due to the plasticization by PPA.

Conclusions

PPA had a prominent effect on the plastification of PVC. It exhibited the lower migration rate in PVC matrix. Thermal and dynamic mechanical analysis revealed that PPA was miscible with PVC. In this study, it indicated that the addition of PPA significantly decreased the tensile strength and increased the elongation-at-break of PVC/PPA blends. Because of the plasticization effect of PPA, in the molten state, the PVC/PPA blends exhibited plastic deformation and lower complex viscosity. These results indicated that PPA could act as an environmentally friendly plasticizer of PVC with good characters.

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