

Evaluating Effects of Biobased 2,5-Furandicarboxylate Esters as Plasticizers on the Thermal and Mechanical Properties of Poly(vinyl chloride)

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ABSTRACT: We synthesized 2,5-furandicarboxylate esters [i.e., dibutylfuran-2,5-dicarboxylate, diisoamylfuran-2,5-dicarboxylate, and di(2-ethylhexyl)furan-2,5-dicarboxylate] and investigated their potential application as plasticizers of commercial poly(vinyl chloride) (PVC) products. Fourier transform infrared analysis, mechanical tests, scanning electron microscopy investigation, differential scanning calorimetry analysis, dynamic mechanical thermal analysis, thermogravimetric analysis (TGA), melt flow rate (MFR) measurement, and plasticizer migration measurements were used to evaluate the comprehensive properties of the blended products. The results of the tensile tests demonstrate that the blends exhibited antiplasticization and flexible plastic characteristics at 10 and 50 phr in PVC, respectively. Moreover, flexural and impact test data indicate that the three types of blends exhibited a similar tendency: the hardness decreased continuously as the amount of plasticizer increased. Their morphology indicated that all of the plasticizers had good compatibility with PVC. The resulting glass-transition temperature of the investigated plasticizers was lower than that of pure PVC, and reduction was largest for the plasticizer with the highest molecular weight. TGA revealed that the thermal degradation of blended polymers occurred in three stages and that all of the blends were stable up to 180°C. Finally, the MFRs of all of the specimens indicated that the addition of a higher concentration of lower molecular weight biobased esters resulted in improved fluidity, but these compounds migrated more easily from the blends. Hence, 2,5-furandicarboxylic acid derived from biomass has potential as a plasticizer. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40938.

KEYWORDS: blends; compatibilization; glass transition; plasticizer; poly(vinyl chloride)

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INTRODUCTION

Phthalate esters (PAEs) are plasticizers used in poly(vinyl chloride) (PVC) materials with applications in food packaging, medical devices, building materials, children's toys, and other common products. However, PAEs can leach out of PAE-containing products and accumulate in organisms. PAEs are metabolized to monophthalate esters in the body and may cause complications due to potential chronic toxicity.^{1,2} Therefore, PAEs have been banned from use in commodity applications by a variety of U.S. and European agencies on the basis of evidence that PAE plasticizers can trigger kidney lesions,³ hepatic tumorigenesis,⁴ reproductive malformations,⁵ and other diseases.^{6,7}

To reduce or prevent the release of PAE plasticizers from products, reactive phthalates,⁸ crosslinking phthalates,⁹ and polymeric phthalates¹⁰ have been synthesized and investigated. However, the accelerated thermal degradation of the crosslinking products and the poor miscibility of reactive and polymeric

products have limited their applications.^{11,12} Currently, there is increasing interest in the use of natural plasticizers that have low toxicity and low migration rates. Compounds that have been investigated include nontoxic citrate esters,^{13,14} modified natural fatty acid esters,^{15,16} and cardanol.¹⁷ Some of these non-PAEs have been commercialized.^{18,19}

The compound 2,5-furandicarboxylic acid (FDCA) is a potential substitute for terephthalic acid (TPA) and phthalic acid, and it is one of the most valuable biorefined products.²⁰ The precursor of FDCA, 5-hydroxymethylfurfural, can be obtained via the dehydration and cyclization of monosaccharides or polysaccharides with water,²¹ an organic phase,²² or an ionic liquid²³ as the solvent. 5-Hydroxymethylfurfural is further oxidized to FDCA with up to 100% recovery.^{24–27} In addition, FDCA-based polymers have been investigated and compared to TPA-based polymers. Gandini et al.²⁸ synthesized poly(ethylene 2,5-furandicarboxylate), whose glass-transition temperature (T_g), melting

temperature, and crystallinity were similar to those of poly(ethylene terephthalate). Jiang et al.²⁹ analyzed the thermodynamic properties of FDCA- and TPA-based polymers in detail and reported that the FDCA-based polymers exhibited satisfactory mechanical properties. A series of copolyesters based on FDCA were also synthesized and characterized by different methods.^{30–32} Avantium³³ developed polyethylene furanoate bottles using YXY technology to compare its CO₂ and O₂ permeation, recycling, and economical performance with that of poly(ethylene terephthalate) bottles.

However, there are very few reports on FDCA ester plasticizers. Sanderson et al.³⁴ only analyzed the T_g of PVC plasticized with FDCA esters with dynamic mechanical thermal analysis (DMTA) and found that all of the esters were more compatible with PVC than with di(2-ethylhexyl) phthalate (DOP). Moreover, unlike phthalates, furan compounds are metabolized during the Krebs cycle.^{35,36}

In this study, three FDCA esters, dibutylfuran-2,5-dicarboxylate (DBF), diisoamylfuran-2,5-dicarboxylate (DIAF), and *di*-(2-ethylhexyl)furan-2,5-dicarboxylate, were synthesized and used to plasticize PVC from 10 to 50 parts per hundred (phr). Fourier transform infrared (FTIR) spectroscopy, mechanical testing, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), DMTA, thermogravimetric analysis (TGA), melt flow rate (MFR) measurement, and migration measurements were used to investigate the comprehensive properties of the blended products.

EXPERIMENTAL

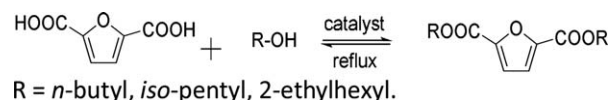
Materials

FDCA was purchased from Chemget Chemical Co., Ltd. (Mianyan, China) and was used as received. The compound 1-sulfobutyl-3-methylimidazolium hydrogen sulfate was supplied by the Center for Green Chemistry and Catalysis at the Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China). *n*-Butyl alcohol, isoamyl alcohol, and 2-ethylhexanol were produced by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). A suspension of PVC (S-1000) with a K (molecular weight of the polymer) value of 66 was obtained from Sinopec Qilu Co., Ltd. (Zibo, China). Zinc stearate and calcium stearate were industrial grade and were used as stabilizers.

Preparation of DBF

n-Butyl alcohol (80 mL), FDCA (10.0 g, 64.1 mmol), and 1-sulfobutyl-3-methylimidazolium hydrogen sulfate as a catalyst (3 wt % FDCA) were added to a flask with a mechanical stirrer, a thermometer, a Dean–Stark trap, and a condenser. The mixture was refluxed with stirring for a specified time (Scheme 1). After the solid FDCA disappeared, the acid value of the reaction system was detected according to ref. 37, and the reaction was halted when the acid value was a small constant. We obtained the target product by filtering out the catalyst, neutralizing the reaction solution, washing the product with deionized water and 2 wt % activated carbon decoloring 2 h at 60°C, removing the excess alcohol *in vacuo*, and drying.

Yield = 99.32%, mp = 42.26°C. ¹H-NMR [400 MHz, hexadeuterated dimethyl sulfoxide (d_6 -DMSO), δ , ppm]: 7.41 (s, 2H), 4.26–



Scheme 1. Esterification of FDCA with different alcohols ($R = n$ -butyl, *iso*-pentyl, or 2-ethylhexyl).

4.32 (t, 4H), 1.62–1.72 (m, 4H), 1.34–1.44 (m, 4H), 0.88–0.96 (t, 6H). IR (KBr, pellet, cm^{-1}): 3154, 3119, 2961, 2931, 2870, 1728, 1576, 1472, 1393, 1289, 1230, 1032, 972, 859, 722. High Resolution Mass Spectrometer (HRMS) [mass-to-charge ratio (m/z): Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_5$, 291.1208; found, 291.1195 $[\text{M}+\text{Na}]^+$.

The purity obtained with the normalization method was 98.11%, as determined by gas chromatography.

Preparation of DIAF

DIAF was prepared under the same reaction conditions as those described previously for DBF, except that *n*-butanol was replaced with isoamyl alcohol.

Yield: 98.75%, mp = 26.34°C. ¹H-NMR (400 MHz, d_6 -DMSO, δ , ppm): 7.39 (s, 2H), 4.28–4.35 (t, 4H), 1.55–1.62 (m, 2H), 1.27–1.34 (m, 4H), 0.90–0.94 (d, 12H). IR (KBr, pellet, cm^{-1}): 3153, 2138, 2960, 2872, 1717, 1577, 1468, 1390, 1276, 1230, 1032, 975, 857, 770. HRMS (m/z): Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_5$, 319.1521, found 319.1509 $[\text{M}+\text{Na}]^+$.

The purity obtained with the normalization method was 92.53%, as determined by gas chromatography.

Preparation of Di(2-ethylhexyl)furan-2,5-Dicarboxylate (DEHF)

DEHF was prepared with the same reaction conditions described previously for DBF, except that *n*-butanol was replaced with 2-ethylhexanol.

Yield: 90.24% d, mp = 7.66°C. ¹H-NMR (400 MHz, d_6 -DMSO, δ , ppm): 7.39 (s, 2H), 4.18–4.22 (d, 4H), 1.60–1.70 (m, 2H), 1.20–1.41 (m, 8H), 0.82–0.92 (t, 12H). IR (KBr, pellet, cm^{-1}): 3122, 2960, 2930, 2867, 1722, 1581, 1463, 1384, 1275, 1223, 1018, 975, 825, 766. HRMS (m/z): Calcd for $\text{C}_{22}\text{H}_{36}\text{O}_5$, 403.2460; found 403.2453 $[\text{M}+\text{Na}]^+$.

The purity obtained with the normalization method was 94.56%, as determined by gas chromatography.

Preparation of the PVC/FDCA Ester Composites

A blend of PVC (100 phr), zinc stearate (0.3 phr), calcium stearate (2.5 phr), and plasticizer (10, 30, or 50 phr) was premixed in a high-speed mixer (Zhangjiagang Hongyun Machinery Co., Ltd., Suzhou, China) at 80°C to produce PVC composites. The composites were then mixed with a two-roll mill (Shanghai Rubber Machinery Works, Shanghai, China) at 180°C for 10 min. After the blends were obtained, 1 and 4 mm thick sheets were compression-molded at 180°C for 15 min; this was followed by cooling to room temperature under a pressure of 10 MPa. The specimens were then stored in sealed plastic bags in air before analysis.

Sample Characterization

FTIR Spectroscopy. FTIR analyses were carried out with a Nicolet 380 FTIR spectrometer (Thermo Nicolet). The spectra

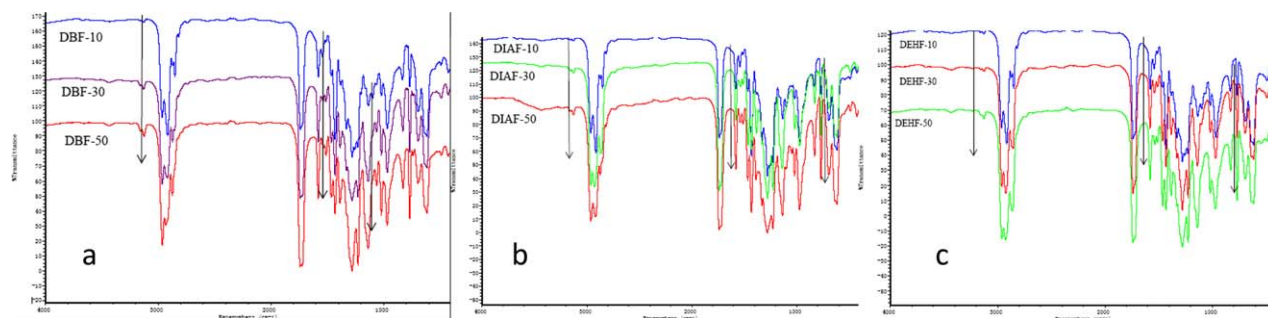


Figure 1. FTIR spectra of PVC plasticized with different FDCA esters: (a) DBF, (b) DIAF, and (c) DEHF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were acquired in the range $4000\text{--}500\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} and were obtained by direct measuring and recording of the IR absorption of the sample films.

Mechanical Properties. Test specimens were cut from the sheets more than 24 h after curing. Tensile and flexural tests were determined at room temperature with a CMT 5254 type electro-mechanical universal testing machine (Shenzhen SANS Testing Machine Co., Ltd., China) at constant rates of 5 and 2 mm/min, respectively, according to ASTM D 882 and ASTM D 790. Notched Izod impact strength tests were conducted with an Izod impact tester (UJ-4, Chengde Machine Factory, China) at room temperature in accordance with ASTM D 256. Hardness tests (Shore A/D) were carried out with a hardness tester (XHS-A/D, Yingkou Testing Machine, Co., Ltd., China) according to ASTM D 2240.

SEM Analysis. To investigate the morphology of the specimens, a scanning electron microscope (S-3400N II, Hitachi, Japan) with a working voltage of 10 kV was used to observe the fractured surface of the notched Izod impact specimens in liquid nitrogen. Before viewing, the observed surfaces were coated with gold, and the observation sites were located in the central regions of the surfaces. No staining or any other chemical treatments were used in this study.

T_g . The T_g of the specimens was investigated with a differential scanning calorimeter (Q2000, TA Instruments). The specimens were approximately 6 mg in weight. To eliminate the thermal history, two heating runs were performed. Each specimen was first scanned from room temperature to 200°C ; this was followed by cooling to -50°C at a rate of $50^\circ\text{C}/\text{min}$. The second scan, at a heating rate of $10^\circ\text{C}/\text{min}$, was used to determine the T_g value of each specimen. Tests were performed in a nitrogen atmosphere. T_g was defined as the midpoint of the change in the heat capacity on the plot of the second scan.

Dynamic mechanical thermal analyses were conducted with DMTA (Q800, TA Instruments). The analyses were carried out on specimens measuring $15 \times 8 \times 1\text{ mm}^3$ in tensile mode with a temperature ranging from -60 to 150°C at a $3^\circ\text{C}/\text{min}$ heating rate with a frequency of 1 Hz. T_g was taken as the peak in the $\tan \delta$ curve accompanied by a step reduction in the storage modulus.

TGA. Thermogravimetric analyses were carried out with TGA (Q5000IR, TA Instruments) under a nitrogen flow ($75\text{ mL}/\text{min}$)

over the temperature range from room temperature to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$.

MFR. The processability of the polymer blends was studied with a melt flow indexer (XNR-400A, Changchun Second Machinery Factory, China), which was used to measure MFR according to ASTM D 1238. The tests were carried out at 190°C after preheating for 5 min under a 15-kg load.

Migration Tests. Migration tests were carried in *n*-hexane according to the guidelines of ASTM D 5227. This test was an extraction/gravimetric method in which the specimens were immersed in *n*-hexane at a constant temperature of 50°C , and after a specified time, the weight loss was measured. This method assumed that the weight of the residue extracted into *n*-hexane was equal to the plasticizer extracted from the specimen.

RESULTS AND DISCUSSION

FTIR Analysis

Initially, the PVC specimens were characterized with FTIR spectroscopy. The FTIR spectra shown in Figure 1 provided evidence for the similar chemical structures of the three types of plasticizers. Interactions between the functional groups in the blends caused the characteristic vibration peak drift. For the DBF-plasticized PVC specimen, for example, the characteristic absorptions of the furan ring occur at 3154 , 3119 , 1576 , 1032 , 972 , 859 , and 722 cm^{-1} , and that of the ester carbonyl appears at 1728 cm^{-1} .²⁸ The absorptions at 2961 , 2870 , 1393 , and 1230 cm^{-1} were assigned to the methyl of *n*-butyl ester group vibrations. The absorptions at 2931 and 1472 cm^{-1} were ascribed to the methylene units of the *n*-butyl group and PVC, respectively. The absorption of the C—O group appeared at 1289 cm^{-1} , and the C—Cl stretching vibration of the PVC was observed at 616 cm^{-1} . With an increase in the DBF content, the peak height of the characteristic absorption at 616 cm^{-1} increased significantly, as shown in Figure 1(a). The FTIR spectra of the other specimens could be explained similarly. However, in our system, no obvious shifts to lower wave numbers were observed. This result indicated that strong specific interactions and chemical reactions between the plasticizers and PVC in the various blends did not occur.

Mechanical Properties

The mechanical properties of the blends are shown in Figure 2 and Table I. The tensile and flexural strength results are

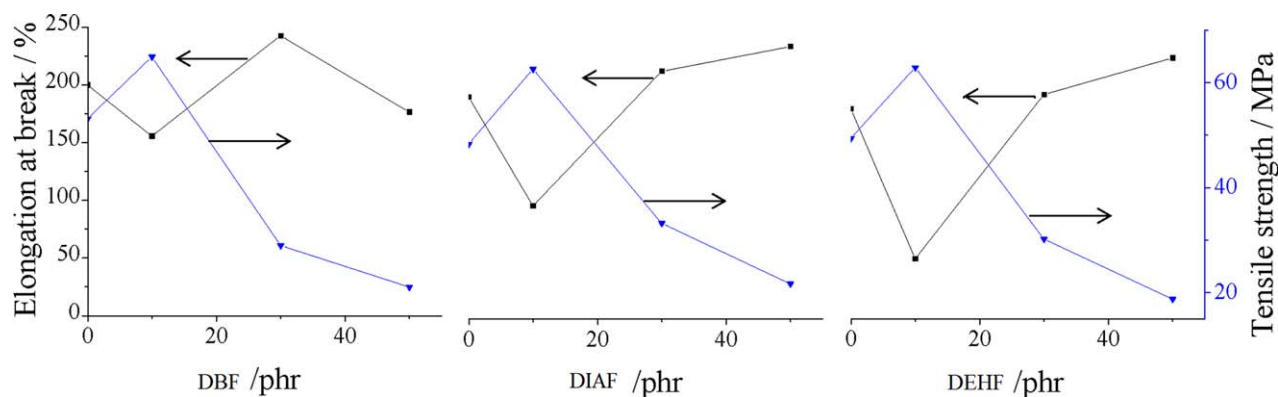


Figure 2. Effects of different FDCA ester plasticizers on the tensile strength and elongation at break of PVC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

depicted in Figure 2, whereas the results of the notched Izod impact strength and hardness tests of the blends are presented in Table I.

As shown in Figure 2, with increasing FDCA ester content, the tensile strength of the blends increased from 11.48 MPa (DBF), 17.92 MPa (DIAF), and 18.75 MPa (DEHF) at 10 phr to 63.34, 66.29, and 62.89 MPa at 50 phr, respectively. However, the tensile strength of the PVC without added plasticizer was reported to be 49.4 MPa.³⁸ Meanwhile, the elongation at break of the three blends types at 10 phr was lower than that of pure PVC. With increasing FDCA ester content, the elongation at break of all of the blends also increased, but that of the PVC plasticized with DBF at 50 phr remained lower than that of PVC. On the basis of these results for the tensile strength and elongation at break, we concluded that all of the blends at 10 phr experienced an antiplasticization effect because of the addition of the FDCA esters. This antiplasticization behavior could be explained by the formation of secondary bonds, such as hydrogen bonds and van der Waal's interactions, between the molecules of the additive and PVC. The penetration of the plasticizer through the PVC matrix caused a partial relaxation of the PVC chains via the reduction of the intermolecular force of attraction; this pro-

vided a greater freedom of movement among the PVC. Therefore, the result of adding the plasticizers was a marked decrease in the tensile strength and a considerable increase in the elongation at break due to the reduced interactions between the PVC molecules.³⁹ With DBF, when the concentration increased to 50 phr, the flexibility of the blend was promoted, but the lower molecular weight of this FDCA ester decreased the adhesion between the DBF and PVC, and increased the degree of solvation of the blend. When concentration of plasticizer increased, the motion of molecular chains was easier, and the physical crosslinking point of the polymer was more decentralized; as a result, the strain of the blends was attenuated, and the elongation at break decreased.⁴⁰ Consequently, the elongation at break declined. However, when the concentrations of DIAF and DEHF increased, the rate of increase in the tensile strength and elongation at break of the blends with these FDCA esters was reduced.

When the content of FDCA esters was increased to 50 phr, the PVC blends changed from rigid to flexible. The results of flexural tests on the blends are shown in Table I. As the amount of FDCA esters increased in DIAF or DEHF-plasticized PVC, the flexural strength and flexural modulus of the blends first

Table I. Mechanical Properties of PVC Plasticized with Different Concentrations of FDCA Esters

Plasticizer	phr	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (kJ/m ²)	Shore	
					D	A
None	0	76.2	2706	3.6	33	
DBF	10	92.34	3419.31	2.59	78	
	30	8.84	330.19	4.51	65	
	50	N	N	N		81.5
DIAF	10	70.53	2674.05	2.32	77.5	
	30	2.62	56.06	4.35	73	
	50	N	N	N		87.5
DEHF	10	90.21	3350.48	2.38	81.5	
	30	16.9	708.41	3.46	87.5	
	50	N	N	N		89

N, not detected.

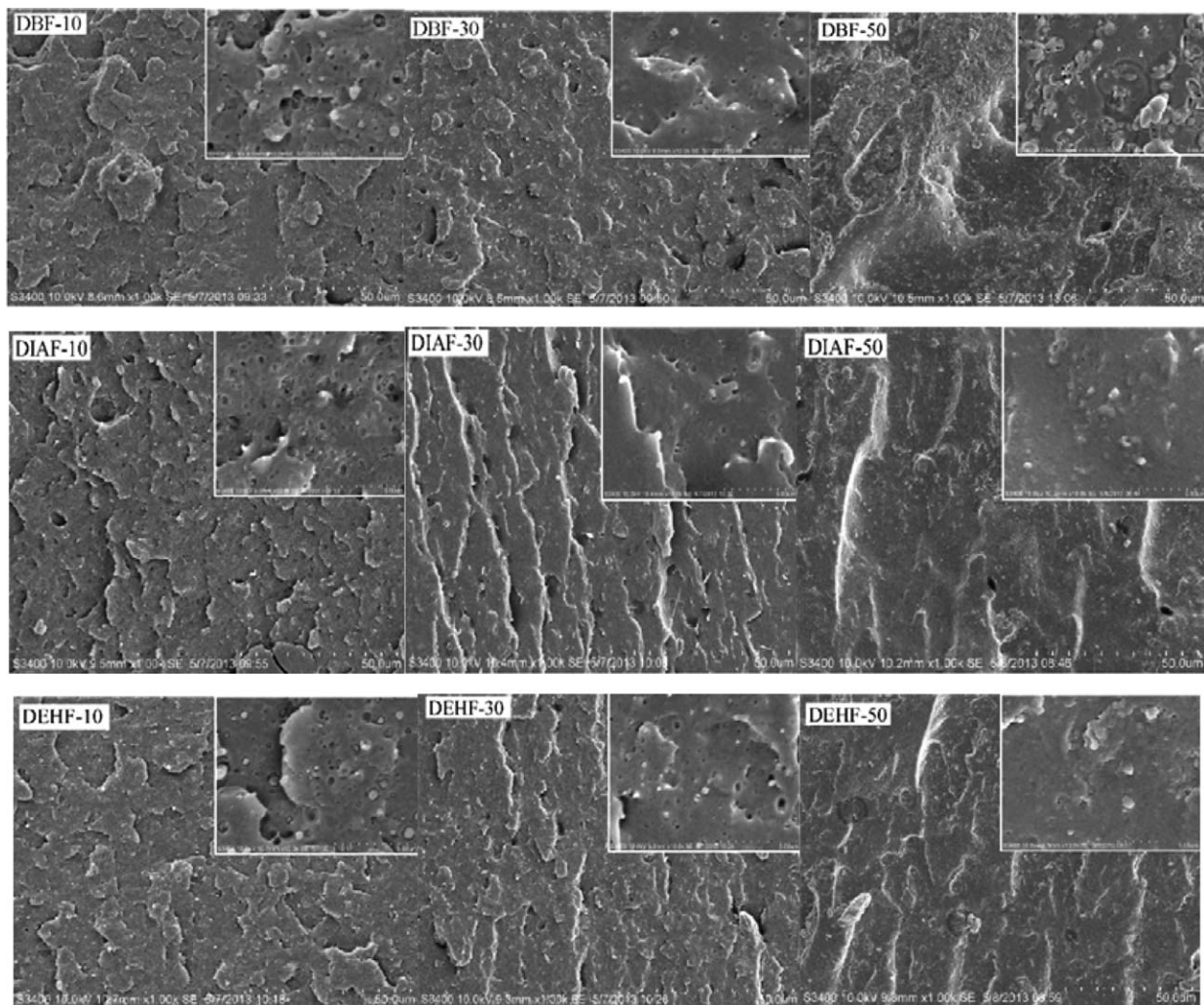


Figure 3. Effects of different FDCA esters at various dosage levels on the morphology of PVC.

increased and then decreased. However, they decreased in the DBF-plasticized PVC. Moreover, as the molecular weight of the esters increased, the flexural strength and flexural modulus of the plasticized PVC blends with the same amount of additive increased from 70.53 and 2674.06 MPa (DBF at 10 phr) to 92.34 and 3419.31 MPa (DEHF at 10 phr), respectively.

The impact strength of the three types of plasticized PVC first decreased and then increased with plasticized conclusion (Table I). Moreover, at the same concentration, the impact strength of the high-molecular-weight plasticizer was greater than that of the low-molecular-weight plasticizer because some inhibition in the free rotation around this ester bond, which gave a less flexible compound that was less able to create free volume, such as di(2-octyl)phthalate, that exhibited less efficiency than DOP.⁴¹ This may have been because the plasticizer molecules penetrated into the PVC matrix during addition, and the inner lubrication reduced the force between the PVC molecules and increased the flexibility of the molecular chain.^{42,43} It showed a lower impact strength of the blends and antiplasticization (10 phr). With increasing amount of plasticizer, the accumulation effect occurred between the PVC molecules after supersaturation, so

this increased the tightness of the molecules and showed an external plasticization effect.⁴⁴ This resulted in the increased impact strength of the blends (30 phr).

Finally, as the amount of FDCA esters increased, the hardness of all of the blends was decreased (Table I). Moreover, for the same amount of plasticizer, the blends with the higher molecular weight FDCA ester exhibited higher hardness values. Therefore, we concluded that the FDCA esters not only affected the toughness of the blends but also had a significant influence on the rigidity of the products. It is worth noting that all of tensile and flexural properties, impact strength, and hardness were improved similar to the regulars by the change in the plasticizers.

Morphology

The fractured surfaces of all of the blends were investigated by SEM. The microscopic structures of the PVC specimens plasticized with the three FDCA esters are shown in Figure 3. The profiles of blends with 10 and 30 phr plasticizer had only a few small dispersed particles, mainly because of the gelation of the PVC particles⁴⁵ and the preplasticizing effect of high-speed

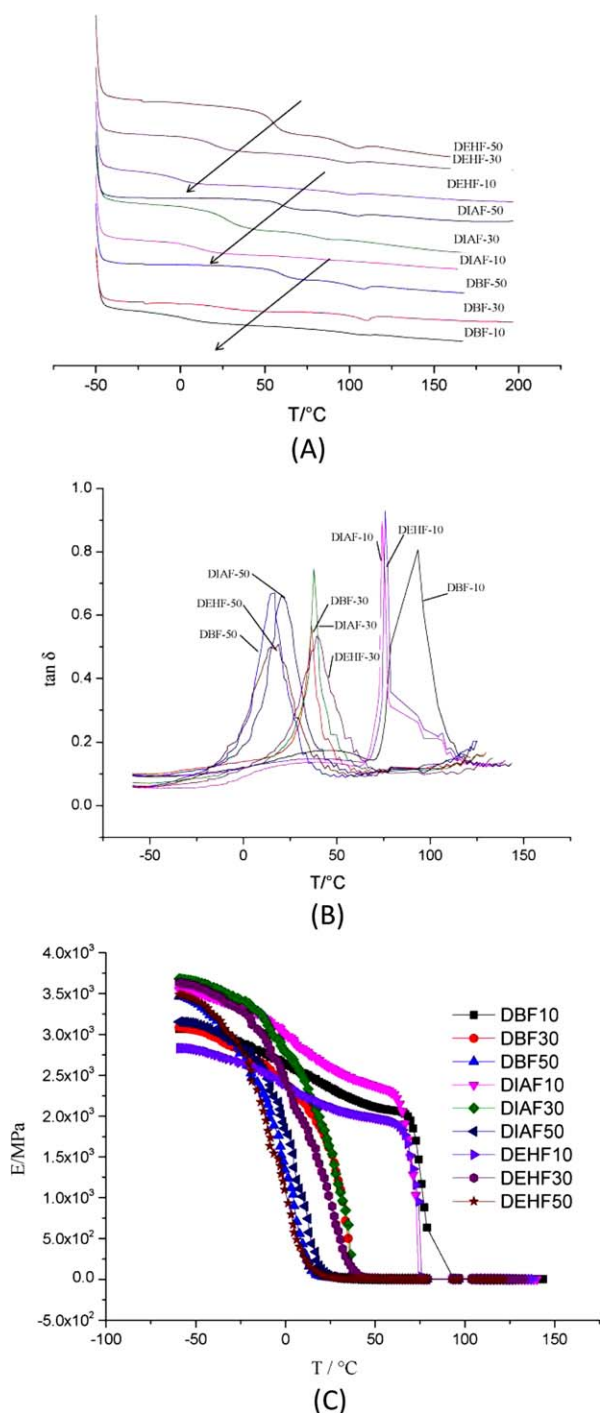


Figure 4. Effects of the FDCA ester concentration on the glass-transition behavior of PVC: (A) DSC, (B) mechanical loss, and (C) storage modulus. E = elastic modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixing and because no other additives were used. However, it is still shown in the figure that as the content of the FDCA esters increased, the quantity of white particles decreased, whereas the tiny overlapping scales observed at the 10-phr addition level gradually increased, thickened, and appeared significantly larger. Thus, the addition of higher concentrations of FDCA esters

resulted in the formation of larger aggregates and reduced interactions between the PVC and plasticizers. This morphological behavior of the FDCA ester based systems could be attributed to a decrease in the matrix viscosity and denoted good plasticizer incorporation into the PVC matrix.

Glass Transition

The T_g values of the PVC specimens plasticized with the FDCA esters were obtained via DSC and DMTA. The DSC and DMTA curves [Figure 4(A,B), respectively] show that the FDCA ester plasticizers were effective at decreasing the T_g values of all of the blends. The T_g values for all of the specimens are listed in Table II. Because the glass transition is a kinetic process, it is affected by the rate at which the sample is heated, and different experimental techniques lead to different T_g values.⁴⁶ This variation is due to different time responses for the motions of the side- and main-chain polar groups and the mechanical or thermal stimulation of this motion.⁴⁷ The T_g values for the blends obtained with DSC were lower than those obtained with DMTA. However, in both cases, T_g decreased dramatically when the plasticizer level was increased from 10 to 50 phr, and the lowest values were observed for the DBF blends. The T_g values determined with DMTA were closer to the actual values for the blends because DMTA is more sensitive than DSC.⁴⁸ The temperature corresponding to the peak value of $\tan \delta$ was clearly T_g [Figure 4(B)].

Finally, as the temperature increased, the storage moduli of all of the blends decreased [Figure 4(C)]. Below T_g the blends had a high storage modulus. However, with an increase in the temperature, the PVC specimens plasticized with different FDCA esters exhibited similar changes in the storage modulus. The reduction of the storage modulus indicated that the blends became more flexible. This enhanced the flexibility results because the hydrogen bonding within the PVC was disrupted; this enabled the activity of the molecular chains to increase. All of these results indicated good miscibility between PVC and the plasticizing agents.

Table II. T_g and Storage Modulus (at 23°C) Values of Poly(vinyl alcohol) Specimens with Different FDCA Ester Concentrations

Sample	Storage modulus ($\times 10^9$ Pa)	T_g (°C)	
		DSC	DMA
DBF-10	2.05	54.60	89.27
DBF-30	0.502	19.39	36.40
DBF-50	0.106	0.49	16.85
DIAF-10	1.03	59.94	74.21
DIAF-30	0.305	27.21	37.72
DIAF-50	0.125	8.30	21.70
DEHF-10	0.953	59.17	75.89
DEHF-30	0.121	26.37	39.23
DEHF-50	0.091	1.15	18.82

DMA, dynamic mechanical analysis.

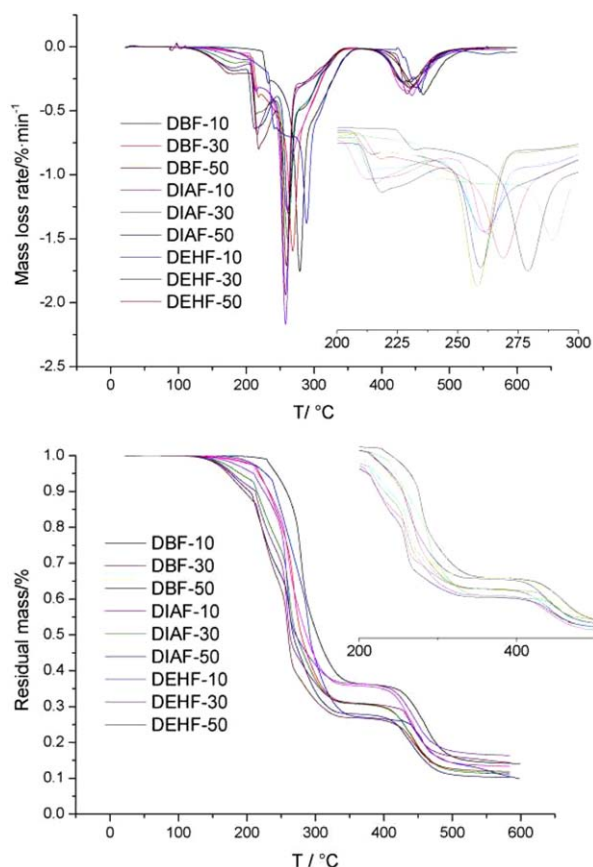


Figure 5. TGA and DTG curves for PVC specimens plasticized with different FDCA esters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Addition, Sanderson et al.³⁴ analyzed the T_g , loss modulus, and storage modulus values of the FDCA esters and DOP-plasticized PVC by DMTA. The results show that when the concentration of the plasticizer increased, the T_g , loss modulus, and storage modulus values of the blends decreased. The compatibility differences of the FDCA esters and DOP with the PVC matrix were determined by quantitative analysis with designed calculation. In this study, the experimental analysis data showed in detail that the conclusion was consistent with Sanderson et al.

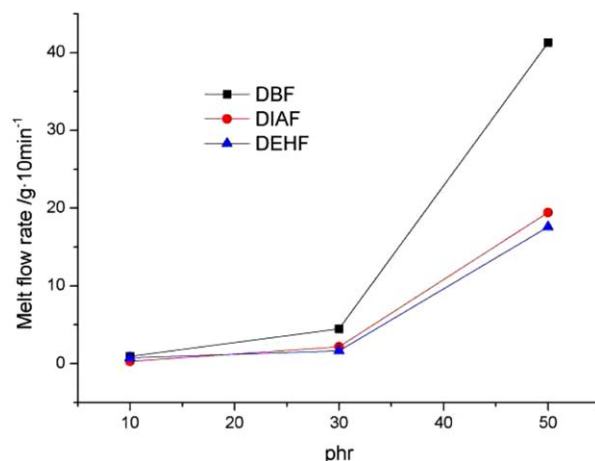


Figure 6. MFR for PVC specimens plasticized with different FDCA esters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TGA

TGA is used to evaluate the thermal stability of different blends.⁴⁹ Dynamic thermogravimetric and derivative thermogravimetric curves for the different PVC specimens are shown in Figure 5. All of the blends exhibited a three-stage degradation, and this was in agreement with the literature.^{50,51} The first stage of weight loss (up to 230°C) was mainly due to plasticizer release and evaporation. As the molecular weight and amount of the plasticizer increased, the weight loss of the blends also increased (Table III). Because the first stage was a continuous process, no clear boundaries between the first and next stage were observed. The second stage (up to 320°C) involved the dehydrochlorination of PVC and the formation of macromolecules with conjugated bonds. Obvious changes in the second peak of the derivative thermogravimetry (DTG) curves were observed. In the third stage (up to 520°C), the polymers with the conjugated bonds formed in the second step underwent cracking and pyrolysis to generate low-molecular-weight linear hydrocarbons. Consequently, the residue of the blends decreased as the concentration and molecular weight of the plasticizers increased.

Table III. TGA Results for PVC Specimens Containing Different FDCA Esters

Plasticizer content (phr)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Weight loss (%)			Residue (%)
				Step 1	Step 2	Step 3	
DBF-10	242.6	257.7	302.6	3.42	60.03	19.55	17.00
DBF-30	233.7	246.8	294.9	5.14	64.22	14.94	15.70
DBF-50	227.9	242.1	292.2	10.55	62.43	14.22	12.80
DIAF-10	232.4	247.7	302.1	5.62	58.37	22.02	13.99
DIAF-30	205.4	230.0	287.5	10.08	59.07	19.25	11.60
DIAF-50	191.7	219.2	283.1	15.51	56.35	17.33	10.82
DEHF-10	225.2	240.4	286.8	7.37	56.31	21.58	14.74
DEHF-30	194.8	227.8	278.3	13.36	55.44	19.44	11.76
DEHF-50	187.6	211.6	275.6	17.76	55.20	12.36	10.65

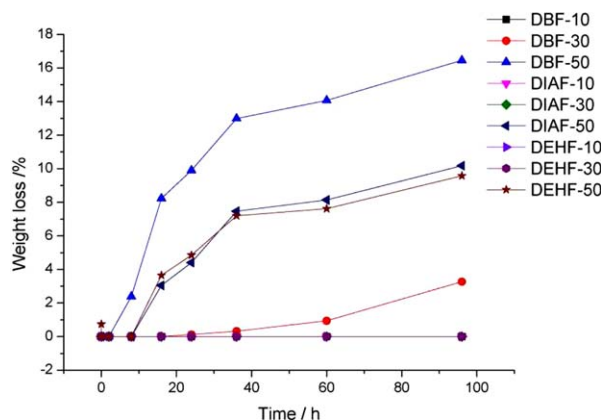


Figure 7. Migration curves for PVC plasticized with different FDCA esters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The detailed results of the TGA are listed in Table III. The $T_{5\%}$, $T_{10\%}$, and $T_{50\%}$ values are defined as the temperatures at 5, 10, and 50% weight loss, respectively. For instance, when the DBF concentration was increased from 10 to 50 phr, the values for $T_{5\%}$, $T_{10\%}$, and $T_{50\%}$ decreased by approximately 5–10°C. Similarly, the thermal stability of the blends with the higher molecular weight esters was lower than that of the blend with the low-molecular-weight DBF at the same plasticizer concentration.

MFR

MFR is used as a tool for quality control and assurance and to provide rapid material characterization, specifically for the evaluation of the quality of the material and the assessment of its processability.⁵² The MFR of the PVC specimens plasticized with the FDCA esters (Figure 6) increased from 0.93 (DBF), 0.74 (DIAF), and 0.29 g/10 min (DEHF) at 10 phr to 41.28, 19.43, and 17.58 g/10 min, respectively, at 50 phr. At high temperatures, the flow cells of the blends enhanced the thermal motion of the polymer chains; this weakened the interactions and reduced the flow impedance. Moreover, as the plasticizer concentration increased, the force between adjacent PVC chains weakened. This led to the formation of separate segments, which resulted in higher mobility of the blends.⁵³

Migration

The migration of plasticizers from flexible plastics to other media is highly dependent on the diffusivity of the plasticizer in

its host polymer, and the diffusivity is decreased by strong polymer–plasticizer interactions.⁵⁴ As shown in Figure 7, the migration of the FDCA esters was a function of the ester concentration and type. When DIAF and DEHF were added at 10 and 30 phr, they were retained well in the PVC blends, and no migration occurred. However, the low-molecular-weight DBF began to migrate after 24 h at 30 phr. In addition, when the plasticizers were added at 50 phr, the migration began at 8, 8, and 16 h for DBF, DIAF, and DEHF, respectively, and did not stabilize until 36 h. In general, a lower molecular weight and a higher amount of the plasticizer facilitated migration of the FDCA esters from the blends.

Comparison of DEHF- and DOP-Plasticized PVC

DEHF and DOP are aromatic esters that contain furan and benzene rings, respectively. To further evaluate the performance of the FDCA esters as plasticizers, the relevant properties of PVC plasticized with DEHF and DOP were compared, as shown in Table IV. Although the use of different test methods and PVC raw materials may have affected the results, the table shows that the tensile strength and elongation at break of the PVC plasticized with DEHF were similar to those of PVC plasticized with a similar amount of DOP.

CONCLUSIONS

Three types of FDCA esters (DBF, DIAF, and DEHF) were synthesized with an environmentally friendly method. Mechanical tests on PVC specimens plasticized with the FDCA esters indicated that antiplasticization interactions and flexible PVC were obtained at ester concentrations of 10 and 50 phr, respectively. In particular, at higher concentrations, the tensile strength and elongation at break increased, whereas the flexural properties and hardness decreased. Moreover, the analysis of the morphology indicated that all of the plasticizers had good compatibility. The T_g , storage modulus, and thermal degradation of all of the plasticizers were found to be lower than those of pure PVC, and the reduction was the greatest for the plasticizer with the highest molecular weight. Notably, the degradation of the blends occurred in three stages. Furthermore, the MFRs of all of the PVC specimens containing the FDCA ester plasticizers indicated that the use of a higher amount of lower molecular weight plasticizers provided better fluidity, but the smaller esters migrated more readily from the blends. Finally, the tensile strength and elongation at break of PVC plasticized with DEHF were found to be similar to those of PVC plasticized with the same amount of DOP.

Table IV. Property Comparison for DEHF- and DOP⁵⁵-Plasticized PVC

	DEHF			DOP		
	10	30	50	10	30	50
Freezing point (°C)		7.66			–55	
phr	10	30	50	10	30	50
Tensile strength (MPa)	62.89	30.21	18.75	59	22	8
Elongation at break (%)	57.09	213.66	248.67	75	301	325
Shore	79 (D)	67 (D)	89 (A)	—	—	79 (A)

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