Evaluation of the Effects of Biobased Plasticizers on the Thermal and Mechanical Properties of Poly(vinyl chloride)

N. Gil,[1] M. Saska,[1] I. Negulescu[2]

[1]Audubon Sugar Institute, Louisiana State University Agricultural Center, St. Gabriel, Louisiana 70776
[2]Department of Human Ecology, Louisiana State University Agricultural Center, Baton Rouge, Louisiana 70803

ABSTRACT: Blends were prepared of poly(vinyl chloride) (PVC) with four different plasticizers; esters of aconitic, citric, and phthalic acids; and other ingredients used in commercial flexible PVC products. The thermal and mechanical properties of the fresh products and of the products after 6 months of aging were measured. Young's modulus of the PVC blends was reduced about 10-fold by an increase in the plasticizer level from 15 to 30 phr from the semirigid to the flexible range according to the ASTM classification, but a 40-phr level was required for PVC to retain its flexibility beyond 6 months. At the 40-phr level, tributyl aconitate performed better than diisononyl phthalate (DINP) or tributyl citrate, in terms of lowering Young's modulus, both in the fresh materials and those aged for 6 months. The effects of the four plasticizers on the glass-transition temperature (T_g) were similar, with T_g close to ambient temperature at the 30- and 40-phr levels in freshly prepared samples and at 40–60°C in those aged for 6 months. The thermal stability of the PVC plasticized with DINP was superior among the group. Overall, tributyl aconitate appeared to be a good candidate for use in consumer products where the alleged toxicity of DINP may be an issue. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1366–1373, 2006

Key words: mechanical properties; poly(vinyl chloride) (PVC); thermal properties

INTRODUCTION

After polyethylene, poly(vinyl chloride) (PVC) is the most widely used plastic. Some 25–35% of total PVC production goes into flexible consumer products such as wire and cable insulation, flooring, wall covering, and packaging materials. For those applications, before molding or extrusion, PVC must be blended with a suitable plasticizer, a compound designed to weaken intermolecular bonds in the polymer to increase its workability, toughness, and flexibility.[1,2] In addition to its good miscibility with the polymer, other attributes of a good plasticizer include a high boiling point to prevent or reduce its loss during processing and a low rate of migration out of the polymer to avoid loss of its properties[3] and contamination of the materials or consumers in contact with it if it is a part of food-grade or personal use products.

Until now, plasticizers produced from phthalic anhydride, such as diisononyl phthalate (DINP; Fig. 1),

di-2-ethylhexyl phthalate, and diisodecyl phthalate, have been the most widely used. In a recent study,[1] the effects were evaluated of several phthalate plasticizers and their blends on the mechanical, thermal, and electrical properties of PVC. However, growing concerns about their toxicity[4–6] in consumer products made of PVC have led to a search for alternatives that will not elicit the same public health concerns. Alternatives to phthalates have included esters of bioderived citric acid, such as tributyl citrate (TBC), acetyl tributyl citrate (ATBC; Fig. 1), triethyl citrate, acetyl triethyl citrate, and tri(2-ethylhexyl) citrate. The U.S. Food and Drug Administration approved both the acid and its esters as additives in food.[7] Nevertheless, the price of these esters is about three times higher than that of phthalates, and their application is limited to small-niche markets.

Alternatives that were proposed in the past included esters of aconitic (1,2,3-propene tricarboxylic) acid and, in particular, tributyl aconitate (TBA; Fig. 1). Several hundred tons of calcium magnesium aconitate were produced annually in Louisiana from 1946 to about 1956 from byproducts of sugar cane processing.[8,9] No published reports are known to us about the processes that used the aconitate at that time, but its use was presumably based on two U.S. patents,[10,11] which, without much detail, disclosed ways of preparing copolymers of aconitate esters
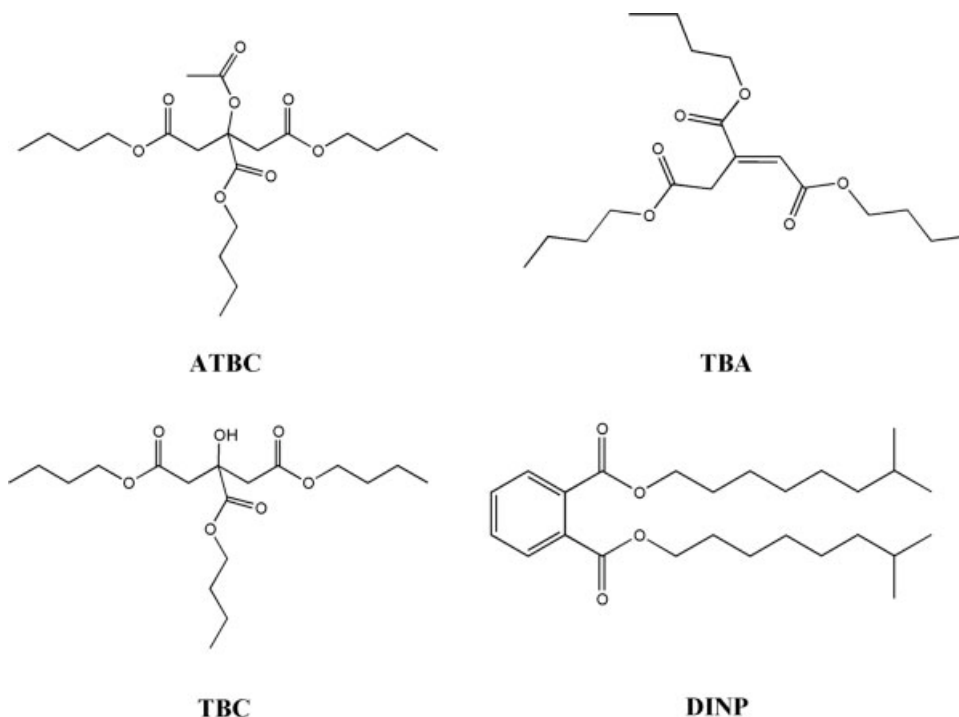
Figure 1 Chemical structure of the four plasticizers and esters of citric, aconitic, and phthalic acids.

with PVC. Both the aconitic esters and tricarballylic acid esters (the hydrogenated variants of aconitic esters) were evaluated as vinyl plasticizers in the early 1950s.[12] Among other effects, it was claimed that TBA protected PVC from negative effects of light and heat. Nevertheless, it appears that after several years of production, the market for crude aconitate disappeared, replaced with lower cost esters of sebacic and phthalic acids.

In view of the advances in technologies for recovering aconitic acid from sugar cane,[13,14] which should lower its cost, and the continued need within the sugar cane industry to find alternative products, this study was undertaken to reevaluate the industrial potential of TBA and to provide a comparison of TBA as a PVC plasticizer with TBC, ATBC, and DINP.

EXPERIMENTAL

Transaconitic acid, ATBC, and PVC [number-average molecular weight (M_n) = 60,000, weight-average molecular weight = 106,000] were purchased from Sigma Aldrich (St. Louis, MO). Citric acid monohydrate was obtained from Fisher Scientific (Fair Lawn, NJ), and *n*-butyl alcohol was purchased from Mallinckrodt (Paris, KY). Both were used as received. DINP was donated by Dow Chemical Co. Drapex 6.8 (epoxidized soybean oil) and Mark 6711 (a barium zinc stabilizer) were purchased from Crompton (Hahnville, LA). Calcium stearate and nonoxidized polyethylene homopolymer wax [PE (H)-100] were

obtained from Struktol (Stow, Ohio). Calcium carbonate filler was received from Omta Vermont (Lucerne Valley, CA), and Paraloid K 120 N (stearic acid) was received from Rohm & Haas Co. (Philadelphia, PA).

TBC and TBA were prepared in our laboratory (Auudon Sugar Institute) from the respective acid and alcohol by Fisher esterification with a cation-exchange resin, AG 50W-X4 (100–200 mesh, hydrogen form, Bio-Rad, Sunnyvale, CA) as a catalyst. Thirty grams of the acid, a 50% excess *n*-butanol (52.1 g for citric acid monohydrate and 57.5 g for transaconitic acid), and 4 g of the ion-exchange resin were mixed and boiled in a 250-mL, round-bottom flask at atmospheric pressure under reflux in an arrangement similar to the Dean–Stark apparatus, which allowed for the continuous removal of the water of reaction. After about 1.5 h of boiling, when a temperature of about 140°C was reached and no more water was being produced, the reaction was considered complete. The resin was screened off from the liquid product, and the ester returned in the distillation apparatus and any residual alcohol were removed by heating to about 130°C for another hour *in vacuo*.

The purity of the products was evaluated with an Agilent Technologies (Foster City, CA) 6890 N gas chromatograph with a flame ionization detector and a DB-5 capillary column (30 m, 0.25 μ film) under the following conditions: 0.2% solution in ethyl acetate, oven temperature = 250°C, run time = 32 min, He carrier gas at 30 mL/min, and 2-μL injection volume (Fig. 2). TBC and TBA prepared as described
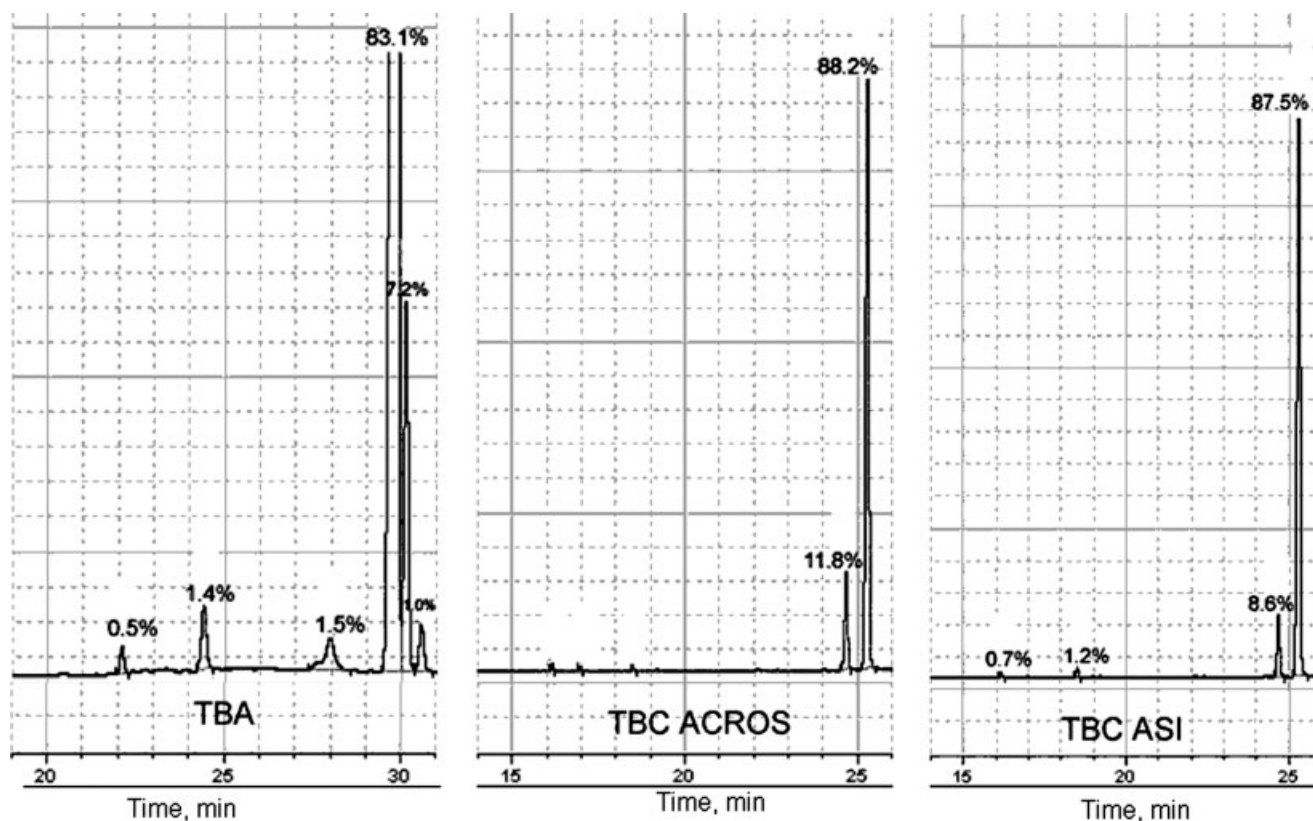
Figure 2 Gas chromatograms of ethyl acetate solutions of TBA and TBC supplied by Acros Organics-Fisher Scientific and TBC-ASI.

previously were used in blends with PVC without any further purification.

PVC plasticization

PVC in a powder form, plasticizers, and other ingredients (Table I) were weighed and mixed according to a modified Large 55 formulation used by the industry.[15] Three series of samples were prepared for each plasticizer at plasticizer-to-PVC ratios of 15 : 100, 30 : 100, and 40 : 100, or 15, 30, and 40 phr, respectively. Fifty-gram batches of the well-mixed ingredients were processed in a Haake (Coesfeld, Germany) torque rheometer at 60 rpm and a temperature between 170 and 180°C. The blending was continued for 15–20 min and stopped when the torque reading dropped and then stabilized after the polymer had melted. The exact blending temperature depended on the plasticizer and its content, but in no case exceeded 180°C. After partial cooling, the polymer was easily removed from the rheometer as small irregularly shaped granules light yellow to light brown in color.

Film preparation

We prepared samples of the PVC films for mechanical and dynamic mechanical analyses by pressing the plasticized polymer granules in a metallic frame with a Carver (Wabash, IN) laboratory press equipped with heated plates. The pressing temperature and pressure for each composition were 180°C and 0.77 MPa for 15 phr, 175°C and 0.62 MPa for 30 phr, and 170°C and 0.48 MPa for 40 phr. The samples were kept in sealed plastic bags at room temperature until testing. After the initial round of tests, the remaining samples were stored for up to 8 months under the same conditions.

Testing

We determined the mechanical properties of the plastics by determining the modulus and ultimate strength in tensile mode with an Instron (Grove City,

TABLE I
Formulations for PVC Plasticization
(grams per 100 g of PVC)

	Plasticizer content (phr)		
Material	Low	Middle	High
Plasticizer	15.0	30.0	40.0
Heat stabilizers			
Drapex 6.8	4.43	5.01	5.40
Mark 6711	1.32	1.49	1.60
Lubricants			
Calcium stearate	0.90	1.02	1.09
PE (H)-100	0.45	0.51	0.55
Paraloid K 120N	0.45	0.51	0.55
Filler: calcium carbonate	17.7	20.0	21.5

PA) tester model 4301 provided with a 1-kN load cell. The crosshead speed was set at 25 mm/min. The sheets were cut into 76.2 mm × 13.5 mm × 1.3 mm strips, as measured with a digital caliper. The samples were conditioned at 21–23°C and 50% relative humidity for at least 40 h before testing.

The glass-transition temperature (T_g) was determined by dynamic mechanical analysis (DMA) in a tensile mode with a Seiko Instruments (Torrance, CA) DMS 200 system with sample films approximately 25 × 7 × 1.3 mm. The film length under tension was 20 mm. The runs were carried out between 25 and 75°C for the low plasticizer ratio and between −30 to 75°C for the middle and high plasticizer ratios with a heating rate of 1°C/min and a train of frequencies from 0.1 to 10 Hz. Alternatively, a TA Instruments (New Castle, DE) DMA Q800 and a AR2000 high-torque rheometer were used for the determination of T_g at the same conditions.

Thermogravimetric analysis was done with a TGA 2950 (TA Instruments) thermobalance to assess the thermal stability of the pure components and of the blends at the standard processing temperatures for plastics. Samples of approximately 10 mg were analyzed in nitrogen with a heating rate of 5°C/min over the 25 to 600°C range.

RESULTS AND DISCUSSION

A plasticizer is a compound incorporated in a polymer matrix to lower its rigidity and improve the properties of the commercial plastic product. Therefore, the addition of the plasticizer often lowers the melt viscosity, T_g, and elastic modulus of the polymer. In a simplified way, the properties and effects of a plasticizer can be compared with those of a solvent. A solvent (or plasticizer) for a given polymer may be judged by either of two separate standards, one kinetic and the other thermodynamic. A kinetically good solvent (plasticizer) is one that will dissolve (in) the polymer rapidly. In the thermodynamic sense, a good solvent (plasticizer) must be capable of strong interactions with the polymer. Thermodynamics dictate that a compound will be a solvent for a particular polymer when the free energy of solution (F) is negative. The factors that contribute to F, temperature (T), enthalpy (H), and entropy (S), are related by the familiar equation

$$\Delta F = \Delta H - T\Delta S$$

Because of the many degrees of local motion permitted to an amorphous polymer, its S of solution usually is small but positive, and the sign of ΔF depends on the magnitude of ΔH. H of mixing, that is, the overall heat of mixing for two liquids, is given by the Hildebrand's equation:[16]

$$\Delta H = \phi_s\phi_p(\delta_s - \delta_p)^2$$

where ϕ_s and ϕ_p are the volume fractions of the solvent and polymer, respectively, and δ_s and δ_p are their respective solubility parameters. It is obvious that as $(\delta_s - \delta_p)^2$ approaches 0, dissolution or, in this case, incorporation of the plasticizer in the polymer matrix is assured by the s factor. One may, therefore, conclude that as a requirement for the solubility of polymer in a solvent or vice versa when the plasticizer is substituted for the solvent, $(\delta_s - \delta_p)^2$ has to be small.

The molecular weights of PVC and the plasticizers used in this study, the polarity reflected by the dielectric constant, and the solubility parameter were used as predictors of compatibility between PVC and the plasticizer (Table II). Although the dielectric constants of TBC and ATBC were quite different and higher than those of PVC, DINP, and TBA, their solubility parameters were similar and close to that of PVC. In the case of TBA, both the dielectric constant and the solubility parameter were very close to, if not the same, as those of PVC. DINP had a dielectric constant between that of the PVC and of the citric esters; however, with the $(\delta_s - \delta_p)^2$ criterion, it should have the lowest miscibility in PVC. These data, even if not exact because of the approximations made in the calculation of the solubility parameters, are very encouraging and point to the fact that the biobased esters considered in this study should behave at least as well as DINP in plasticizing PVC.

TABLE II
Predictors of Compatibility of Plasticizers and PVC

Materials	M_n	Molecular formula	Dielectric constant	Solubility parameter $(J/cc)^{1/2}$
PVC	60,000	$(C_2H_3Cl)_n$	3.13,[a] 3.10[17]	19.4[17]
TBA	342.2	$C_{18}H_{30}O_6$	3.02[a]	19.4[b]
ATBC	402.3	$C_{20}H_{34}O_8$	6.05[17]	18.4[17]
TBC	360.2	$C_{18}H_{32}O_7$	10.00[17]	18.5[17]
DINP	418.3	$C_{26}H_{42}O_4$	4.64[17]	15.7[b]

[a] Calculated by assimilation of groups.[16]

[b] Calculated as the ratio between the product of the density and the molar attractions constants and the molecular weight of the materials.[2]

TABLE III
Weight Loss in the PVC/Plasticizer Blends

| Plasticizer | phr | Weight loss (%) | | |
		100°C	150°C	200°C
TBA	15	0.11	0.38	1.90
	30	0.15	0.51	3.82
	40	0.31	0.86	5.97
ATBC	15	0.07	0.16	1.09
	30	0.05	0.21	2.42
	40	0.26	0.64	4.99
TBC	15	0.19	0.49	2.67
	30	0.15	0.49	3.43
	40	0.18	0.87	6.19
DINP	15	0.03	0.08	0.38
	30	0.01	0.08	0.51
	40	0.05	0.23	0.97

Thermal stability of plasticized PVC

The weight loss for all blends at 100, 150, and 200°C is given in Table III. The data at temperatures above 200°C are not shown as they are not relevant for processing PVC. If one assumes that the plasticizer is the only component of the blend responsible for the weight reduction, its loss at 200°C was significant. The loss was proportional to the level of the plasticizer in the PVC blend.

At 170°C, the actual processing temperature for the 40-phr formulations, the weight loss from pure PVC and the 40-phr DINP blend (Fig. 3) was around 0.30%, whereas the weight loss from the PVC blended with TBC and TBA was between 1.4 and 1.9%.

The onset temperature was defined as the intersection of the extension of zero weight thermogravimetry loss line with the tangent to the thermogravimetry curve drawn at the temperature corresponding to the highest rate of weight loss, that is, the tempera-
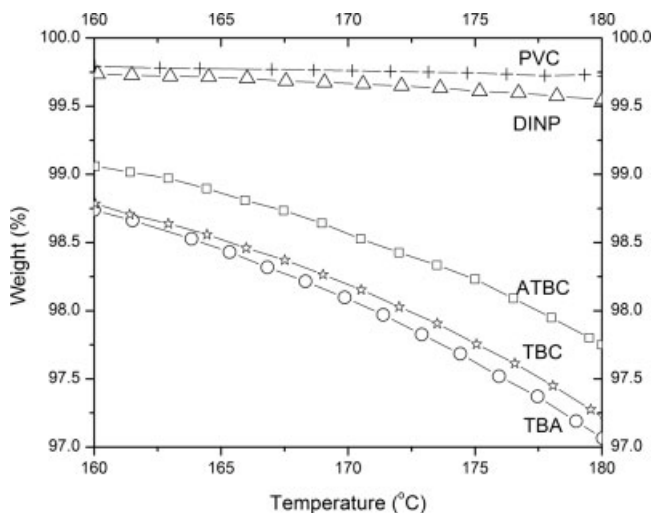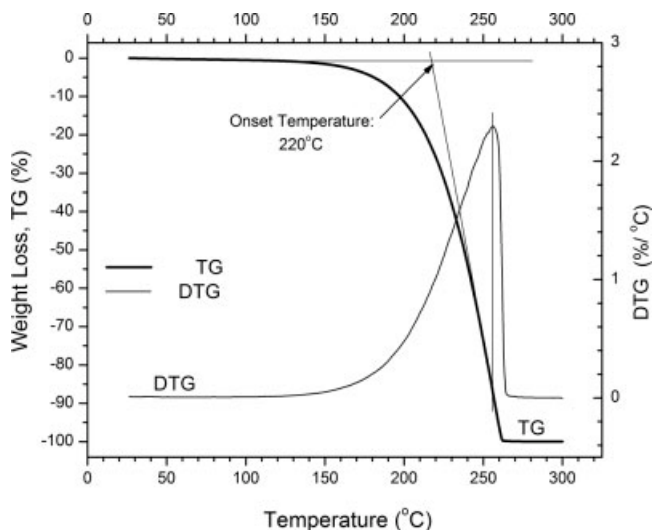

Figure 4 Graphical definition of the onset temperature.

ture of the maximum on the dynamic thermogravimetry (DTG) curve (Fig. 4).

The boiling points of these esters were very high (234°C at 17 mmHg for TBC, 174°C at 1 mmHg for ATBC, 246°C at 5 mmHg for DINP,[17] and 126°C at 0.1 mmHg for TBA[12]), and we, therefore, expected that at atmospheric pressure, the onset temperature in these blends referred mostly to the thermal degradation of the esters.

The onset temperature of the PVC blends plasticized with any of the esters at 15 phr was some 20–25°C higher than the onset temperature of pure PVC (251°C) because of the effect of heat stabilizers in the PVC/plasticizer blends. The effect of the plasticizers was to lower the onset temperature of PVC blends. After 6 months, the onset temperature in the same samples increased, presumably as a result of plasticizer migration. The largest changes were observed in the PVC/DINP blends with 40 phr plasticizer (Table IV).

Figure 3 Weight loss in pure PVC and PVC–plasticizer blends at 40 phr in the range of temperatures in the industrial processing of PVC.

TABLE IV
Changes in the Onset Temperature of the Fresh PVC Samples and the PVC Samples Aged for 6 Months

| Plasticizer | phr | Onset temperature (°C) | | |
		Fresh samples	After aging	Difference
TBA	15	276	283	7
	30	266	279	13
	40	263	272	9
ATBC	15	273	282	9
	30	258	275	17
	40	248	267	19
TBC	30	258	276	18
	40	257	274	17
DINP	15	275	285	10
	30	266	279	13
	40	254	278	24

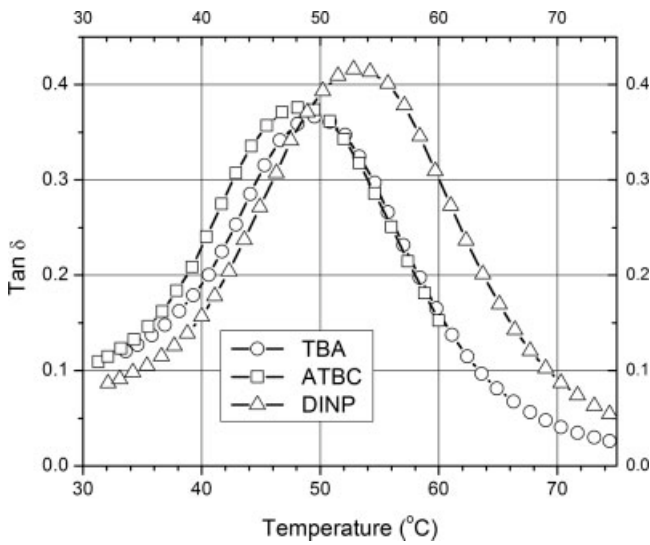**Figure 5** T_g's (maxima of the tan δ curves) of the fresh PVC blends made with 15 phr plasticizer (Seiko Instruments DMS 200 at 1 Hz).

DMA

The actual values of dynamic mechanical characteristics of materials are related both to the temperature and frequency of the determination. According to the superposition time (frequency)–temperature principle, a certain transition, such as the glass transition, can have a multitude of values, each one corresponding to a certain frequency.[18] Figures 5–7 show the variations of tan δ (the ratio between the viscous and elastic moduli) as a function of temperature at 1 Hz for the four PVC samples containing 15, 30, and 40 phr levels of plasticizers, respectively. The T_g values that correspond to the maxima of the curves
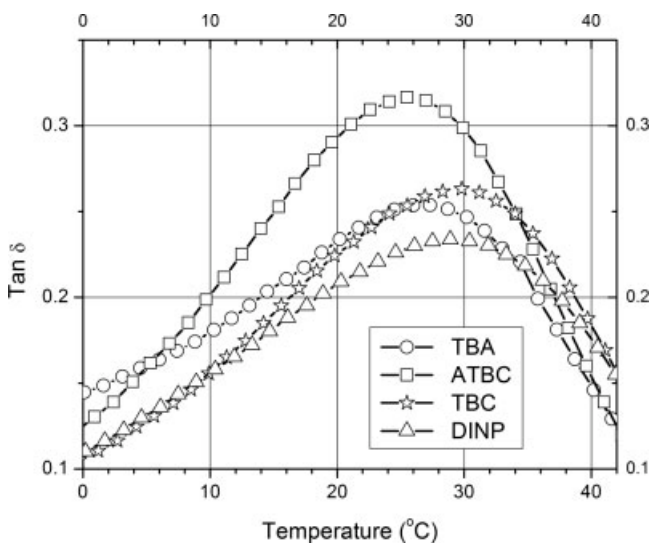

Figure 6 T_g's (maxima of the tan δ curves) of the fresh PVC blends made with 30 phr plasticizer (Seiko Instruments DMS 200 at 1 Hz).

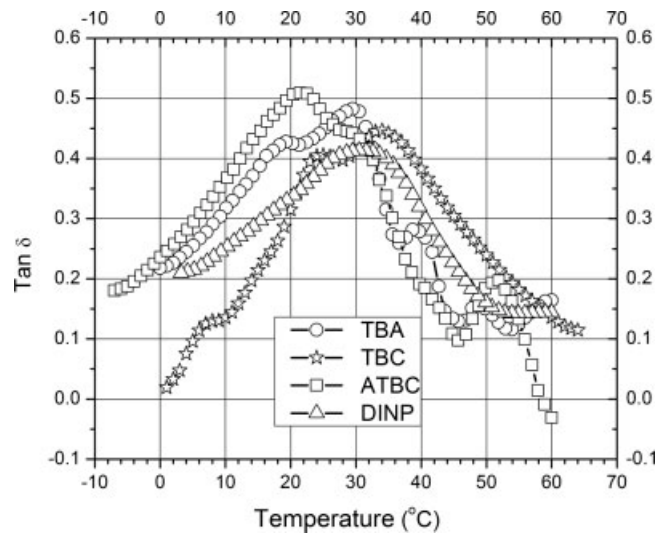**Figure 7** T_g's (maxima of the tan δ curves) of 3-month-old samples with 40 phr plasticizer (AR 2000 rheometer at 1 Hz).

were grouped in a narrow 5°C temperature range at 15 and 30 phr, but a wider range of T_g's was observed at 40 phr.

T_g decreased dramatically when the plasticizer level was increased from 15 to 30 phr with the lowest value found for the ATBC blends.

As a rule, narrow peaks of the tan δ versus temperature curves indicate good miscibility between PVC and the plasticizing agent.[1] In our experiments, the peaks generally became broader as the plasticizer level increased. The tan δ dependence of the 15-phr TBA sample exhibited the narrowest peak, whereas the opposite was found for the 15-phr DINP blend, in good agreement with the solubility values listed in Table II. At 30 phr, the width of all peaks became larger (Fig. 6). At 40 phr, the curves of biobased plasticizers exhibited multiple maxima (Fig. 7). The major peak was taken as T_g (Table V), but one could

TABLE V
Frequency Effect on T_g Values at Low and Middle Plasticizer Ratios

Plasticizer	phr	0.1 Hz	T_g (°C)		
			1 Hz	5 Hz	10 Hz
TBA	15	46	50	52	54
	30	23	27	30	32
	40	—	30	—	—
ATBC	15	45	48	52	54
	30	20	26	30	32
	40	—	22	—	—
TBC	30	25	30	33	34
	40	—	32	—	—
DINP	15	49	53	57	59
	30	24	29	33	35
	40	—	31	—	—

TABLE VI
Changes in T_g at 1 Hz as a Result of PVC Aging for 6 Months at Ambient Temperature

Plasticizer	phr	T_g (°C) Fresh	Aged	Change (%)
TBA	15	50	58	16
	30	27	44	63
	40	30[a]	33	10
ATBC	15	48	60	25
	30	26	40	54
	40	22[a]	31	41
TBC	30	30	48	60
	40	32[a]	38	19
DINP	15	53	62	17
	30	29	49	69
	40	31[a]	35	13

[a] Three months old.

also consider the minor peaks as glassy transitions. Because of instrumental problems, the 40-phr samples were only measured 3 months after they were prepared on an AR2000 rheometer, and some plasticizer migration within this period may have occurred. Multiple peaks were also observed in the same samples (biobased plasticizers at 40 phr) after 6 months (not shown), measured with a TA Instruments Q800. DINP at 40 phr and all samples at 15 and 30 phr showed only one maximum, both in the fresh samples and those aged for 6 months.

After aging, T_g values increased by up to 20°C (Table VI). This behavior is associated with the progressive loss of elasticity of the blends during aging.

The effect of the frequency of DMA measurement (Table V) was well fitted with a power model (Fig. 8).
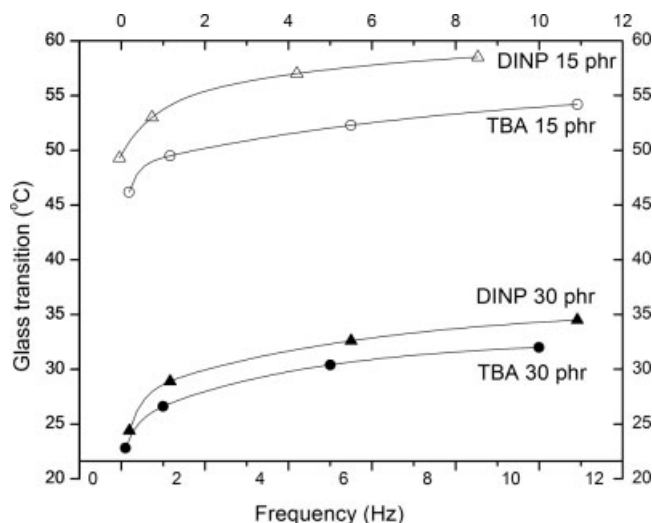

Figure 8 T_g at different frequencies of the fresh PVC samples plasticized with TBA and DINP at 15- and 30-phr levels.

Tensile properties

Polymeric materials are classified by ASTM as rigid if Young's modulus is above 700 MPa (the case of unplasticized PVC), semirigid if it is between 70 and 700 MPa, and soft if it is below 70 MPa.[19] In agreement with this classification, our blends with a low plasticizer level were semirigid and were soft at higher levels. When the content of the plasticizer was doubled from 15 to 30 phr, the modulus dropped roughly 10 times and then decreased about twofold as the plasticizer content increased from 30 to 40 phr (Table VII).

The tensile stress data shown in Table VIII represent the maximum stress supported by the plastics. The trend was similar to that of Young's modulus; that is, the tensile stress decreased as the plasticizer content increased. However, the strength decreased gradually from 30 to 33 MPa for the low ratio to 22–27 MPa for the middle ratio and 20–21 MPa for the 40-phr samples. The small differences in tensile data between the middle and high plasticizing ratio samples pointed to the saturation of PVC with the plasticizer, regardless of its nature. TBC at 30 phr displayed, however, a slightly increased strength (higher tensile stress) compared with the other compositions.

If one considers the Young's modulus data, the situation changed, however, after aging. The modulus increased in all formulations, the least for the low plasticizer ratio blends (Table VII). If the change of Young's modulus with age was used as a relative measure of the plasticizer migration, the results indicate that TBC was more prone to migration followed by TBA, ATBC, and DINP. At the same time, the ASTM classification of the 30-phr plasticized blends changed from soft to semirigid. A noticeable decrease in the tensile stress occurred after aging only in the 15-phr blends. The other compositions remained within the same limits of tensile strength.

TABLE VII
Young's Modulus of the Plasticized Fresh PVC Samples and the PVC Samples Aged for 6 Months

Plasticizer	phr	Modulus (MPa) Fresh	Aged	Change (%)
TBA	15	455 ± 60	569 ± 74	25
	30	42 ± 7	124 ± 22	196
	40	12 ± 0.2	26 ± 2	114
ATBC	15	479 ± 29	561 ± 34	17
	30	31 ± 2	81 ± 6	162
	40	14 ± 1	19 ± 1	40
TBC	30	44 ± 0.4	174 ± 12	300
	40	25 ± 4	84 ± 10	236
DINP	15	473 ± 64	562 ± 24	19
	30	54 ± 5	126 ± 15	132
	40	23 ± 1	36 ± 6	54

TABLE VIII
Stress at the Break Point (Tensile Stress) of the Plasticized Samples

| Plasticizer | phr | Stress (MPa) | | |
		Fresh	Aged	Change (%)
TBA	15	33.2 ± 0.5	27.1 ± 0.2	−18.4
	30	22.2 ± 0.6	20.4 ± 0.4	−8.1
	40	20.4 ± 0.7	20.6 ± 0.6	1.0
ATBC	15	29.8 ± 3.0	27.7 ± 2.5	−7.0
	30	24.0 ± 2.1	25.0 ± 0.5	4.2
	40	20.0 ± 0.8	20.2 ± 1.0	1.0
TBC	30	27.3 ± 0.6	25.8 ± 1.0	−5.5
	40	21.2 ± 3.2	19.8 ± 1.5	−6.6
DINP	15	32.1 ± 1.4	27.3 ± 0.6	−15.0
	30	21.3 ± 1.6	22.2 ± 2.8	4.2
	40	20.8 ± 0.1	20.3 ± 1.1	−2.4

CONCLUSIONS

As expected from the closeness of the dielectric constant and solubility parameters, the biobased esters tested in this study had the same capacity as DINP as plasticizers in PVC. Young's modulus of the PVC blends with any of the four plasticizers decreased about 10-fold with an increase in the plasticizer level from 15 to 30 phr, from the semirigid to flexible range in the ASTM classification. A 40-phr level was required, although, for PVC to retain its flexibility beyond 6 months. At 40 phr, TBA performed better than DINP and TBC and yielded a flexible PVC with a lower Young's modulus, both in the freshly produced samples and in those aged 6 months. Changes in the tensile strength with the plasticizer content were less dramatic, and no age effects were noticeable.

The effect of the four plasticizers on T_g of PVC was similar; they lowered T_g to close to ambient temperature at 30 and 40 phr in fresh samples and to between 40 and 60°C after 6 months. The thermal stability of the PVC plasticized with DINP was superior among the group, with a less than 1% loss of its weight in the 170–180°C range. PVC blended with the bioderived compounds was less thermally stable, with a weight loss of about 2% at 170°C.

Overall, TBA is a good candidate to substitute DINP in consumer products where the alleged toxicity of DINP is an issue and is comparable to esters of citric acid in its effects in flexible PVC formulations.

References

1. Shah, B. L.; Shertukde, V. V. J Appl Polym Sci 2003, 90, 3278.
2. Brydson, J. A. Plastics Materials; Butterworth Scientific: London, 1982; Chapter 5.
3. Audic, J.; Reyx, D.; Broose, J. J Appl Polym Sci 2003, 89, 1291.
4. Latini, G. Biol Neonate 2000, 78, 269.
5. NIH Complete 9th Report on Carcinogens. http://ehis.niehs.nih.gov/roc/ (revised January 2001).
6. U.S. Environmental Protection Agency. Technology Transfer Network Air Toxics website. Phthalic Anhydride. Washington, DC. http://www.epa.gov/ttn/atw/hlthef/phthalic.html#ref1, accessed July 2005.
7. Johnson, W., Jr. J Toxicol 2002, 21 (Suppl. 2), 1.
8. Balch, R. T. Sugar Bull, Aug 15, 1945, p 197.
9. Godchaux, L., II. Sugar J, April 1949, p 1.
10. Hanson, A. W.; Coggin; C. U.S. Pat. 2,273,262 (1942).
11. Cox, F. W. U.S. Pat. 2,419,122 (1947).
12. Roberts, E. J.; Martin, L. F.; Magne, F. C.; Mod, R. R. Rubber World, Sep 1954, p 801.
13. Blinco, J. L. Ph.D. Dissertation, James Cook University, 2000.
14. Gil, N. J. Ph.D. Dissertation, Louisiana State University, to appear.
15. Titow, W. V. PVC Plastics: Properties, Processing and Applications; Elsevier Applied Science: London, 1990; Chapter 2.
16. Van Krevelen, D. W. Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions; Elsevier: Amsterdam, 1990; Chapter 7.
17. Sears, J. K.; Darby, J. R. The Technology of Plasticizers; Wiley: New York, 1982; Chapter 3 and Appendix.
18. Carreau, P. J.; De Kee, D. C. R.; Chbadra, R. P. Rheology of Polymeric Systems. Principles and Applications; Hanser/Gornder: Cincinnati, OH, 1997; Chapter 5.
19. Stuart, B. Polymer Analysis; University of Technology: Sydney, Australia, and Wiley: New York, 2002; Chapters 5 and 8.