

## Dialkyl furan-2,5-dicarboxylates, epoxidized fatty acid esters and their mixtures as bio-based plasticizers for poly(vinylchloride)

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**ABSTRACT:** Dialkyl furan-2,5-dicarboxylates and epoxidized fatty acid esters (EFAE) of varying molecular weights and volatilities, as well as their mixtures, were investigated as alternative plasticizers for poly(vinylchloride) (PVC). The EFAE utilized were epoxidized soybean oil (ESO) and epoxidized fatty acid methyl ester (e-FAME). All plasticizers were compatible with PVC, with plasticization efficiencies usually increasing with decreasing molecular weights of the plasticizers (except in the case of ESO, which was remarkably effective at plasticizing PVC, in spite of its relatively high molecular weight). In comparison with phthalate and trimellitate plasticizers, the alternatives generally yielded improved balance of flexibility and retention of mechanical properties after heat aging, with particularly outstanding results obtained using 30–50 wt % e-FAME in mixtures with diisotridecyl 2,5-furandicarboxylate. Although heat aging characteristics of the plasticized polymer were often related to plasticizer volatilities, e-FAME performed better than bis(2-ethylhexyl) 2,5-furandicarboxylate, and bis(2-ethylhexyl) phthalate of comparatively higher molecular weights. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42382.

**KEYWORDS:** biomaterials; plasticizer; poly(vinyl chloride)

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### INTRODUCTION

Over the past few years, there has been increased interest in developing and using sustainable plasticizers for modification of poly(vinylchloride) (PVC) to impart flexibility to this polymer, as alternatives to petroleum-derived plasticizers.<sup>1–5</sup> Particularly sustainable PVC plasticizers are bio-based and phthalate-free materials derived from renewable resources such as epoxidized derivatives of natural oils, bio-derived succinate esters and their mixtures.<sup>6–13</sup> Bio-based epoxidized soybean oil is especially useful since it is economically affordable and has been demonstrated to be sufficiently compatible with PVC (even as a single plasticizer, at loadings as high as 83 parts per hundred resin or 44 wt % of the entire formulation), but only when used in combination with appropriate thermal stabilizers to prevent acid catalyzed oxirane ring opening, which in turn leads to incompatibility with the polymer.<sup>6,10–16</sup>

Additionally worth considering are esters of furan dicarboxylic acid (FDCA), since some of these are effective PVC plasticizers<sup>17–19</sup> and the precursor acid can be derived from agricultural residues.<sup>20</sup> In the present work, three different dialkyl furan-2,5-dicarboxylates (also referred to as furan dicarboxylic acid esters, FDAE) were utilized for modification of PVC, of which the following two were novel plasticizers: Diisotridecyl

2,5-furandicarboxylate; and Mixed 2,5-furandicarboxylate (having 50% 2-ethylhexyl, 25% octyl, and 25% decyl substituents). The FDAE materials were designed to be of varying molecular weights, so as to be able to achieve satisfactory properties of plasticized PVC when conditioned at temperatures as high as 136°C. Furthermore, novel mixtures of all three FDAE materials with epoxidized fatty acid esters (EFAE; either epoxidized soybean oil or epoxidized fatty acid methyl ester) have been investigated with a view to obtaining optimal balance of properties in the plasticized polymer, specifically to counteract any loss in plasticization efficiency anticipated from increasing molecular weight of the FDAE employed. Comparisons have also been made with the behaviors of conventional phthalate and trimellitate plasticizers. The aim of this work was to demonstrate that FDAE, EFAE, and their mixtures can effectively be used to replace the incumbent petroleum-derived plasticizers and even improve upon their performances, thus addressing the significant health and global warming concerns associated with the latter class of plasticizers.

### EXPERIMENTAL

#### Materials

The materials used were: OxyVinyls 240F suspension-grade PVC homopolymer (product of OxyVinyls, LP; K-value of 70);

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Satintone SP-33 calcined kaolin clay (as electrical insulation filler); Baeropan MC 90249 KA calcium-zinc mixed metal soap (as heat stabilizer); Irganox 1076 (as antioxidant); Microfine AO9 antimony trioxide (as flame-retardant synergist); three different dialkyl furan-2,5-dicarboxylates (also known as furan dicarboxylic acid esters, FDAE, as plasticizers or coplasticizers); two different epoxidized fatty acid esters (EFAE, as plasticizers or coplasticizers); Bis(2-ethylhexyl) phthalate, 98% (DEHP, as plasticizer; product of Alfa Aesar; molecular weight: 391 g/mol); Diisodecyl phthalate (DIDP, as plasticizer; product of TCI Tokyo Kasei; molecular weight: 447 g/mol); and Tri(2-ethylhexyl) trimellitate (also known as trioctyl trimellitate, TOTM, as plasticizer; Eastman grade; product of Sigma-Aldrich; molecular weight: 547 g/mol).

The EFAE materials used were Plas-Chek 775 epoxidized soybean oil (ESO; product of Ferro Corporation; molecular weight: 1000 g/mol; oxirane oxygen content of 7.2%); and Vikolex 7010 epoxidized fatty acid methyl ester derived from soybean oil (e-FAME, also known as methyl epoxy soyate; product of Arkema; molecular weight: 327 g/mol; oxirane oxygen content of 7.0%).

The FDAE materials investigated were: Bis(2-ethylhexyl) 2,5-furandicarboxylate (FDAE-1; FDCA ester with 2-ethyl-1-hexanol; molecular weight: 381 g/mol); Mixed 2,5-furandicarboxylate having 50% 2-ethylhexyl, 25% octyl and 25% decyl substituents (FDAE-2; FDCA ester with 50/25/25% mixture of 2-ethyl-1-hexanol/octanol/decanol; molecular weight: 410 g/mol); and Diisotridecyl 2,5-furandicarboxylate (FDAE-3; FDCA ester with isotridecyl alcohol; molecular weight: 521 g/mol). The syntheses of the FDAE materials have been described elsewhere.<sup>21,22</sup>

#### Thermal Characterization of Plasticizer Constituents

Thermogravimetry (TG) was conducted in platinum pans under nitrogen (at flow rate of 100 cm<sup>3</sup>/min) by raising the temperature from 30°C to 900°C at a rate of 10°C/min, to determine the mass loss of the plasticizer constituent as a function of temperature.

#### Flexible PVC Composition Studied

The following flexible PVC compositions were made and tested, at plasticizer loading of 52 parts per hundred resin (phr): 57.3 wt % PVC, 30.0 wt % plasticizer (DEHP, DIDP, TOTM, FDAE, EFAE, or FDAE/EFAE mixtures), 6.4 wt % calcined clay, 3.0 wt % heat stabilizer, 0.3 wt % antioxidant; and 3.0 wt % antimony trioxide.

#### Preparation of Flexible PVC Compounds

The plasticizers (or plasticizer mixtures) were preheated to 60°C for at least 60 min and shaken by hand for a few seconds before use. “Dry blends” were first prepared, by absorbing the plasticizer composition in PVC powder, as follows: (a) Mixed all ingredients except plasticizer and clay in a container using a spatula; (b) Warmed up a 40 cm<sup>3</sup> Brabender mixing bowl with sigma blades at 90°C and 40 rpm for 2 min; (c) Added the hand-mixed ingredients to the mixing bowl and mixed for 60 s; (d) Added the plasticizer to the mixing bowl, mixed for 10–20 min, and recorded time for complete plasticizer absorption by visual observation (i.e., “Dry Blend Time”—corresponding to the point at which liquid was no longer visible on the surface

of PVC powder); (e) Added clay and mixed for 60 s; and (f) Stopped mixer and removed the dry blend. Thereafter, the blends were melt-mixed using the same Brabender mixing bowl, but with cam rotors, at 40 rpm and 180°C set temperature for 10 min (from the time of loading). The melt-mixed compositions were removed from the mixer, pressed into thin sheets and allowed to cool to room temperature.

#### Molding and Testing of Flexible PVC Compositions

Specimens for property testing were prepared by compression molding the melt-mixed blends at 180°C (2 min at 3.5 MPa, followed by 3 min at 23.8 MPa) into thin sheets, cooling to room temperature under pressure, and subsequently die-cutting to the desired geometries (except the pieces used for hardness measurements, which were molded to the specified geometry). Properties were measured of unaged specimens (i.e., kept at room temperature of 23°C after molding) and of specimens aged for 7 days at elevated temperatures in an oven (100–136°C). Oven-aging was conducted using a Type II ASTM D5423-93 Testing Mechanical Convection Oven.

Shore A and D hardness values were determined at 23°C, according to ASTM D2240, using unaged specimens of 6.4 mm thickness and 51 mm diameter (average of five measurements).

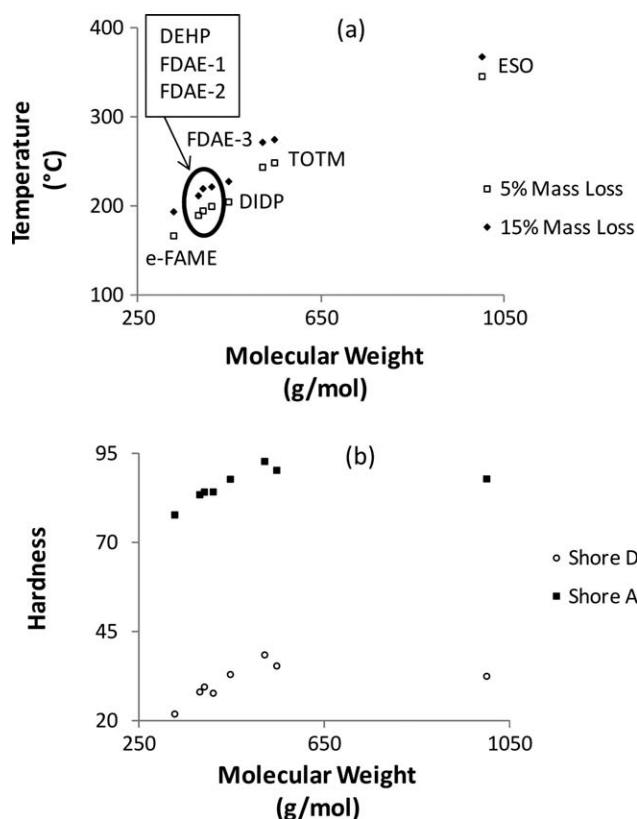
Loop-sprew was measured in accordance with ASTM D3291, to determine if any exudation occurred when unaged specimens of 2 mm thickness were bent for 48 h at 23°C, as an assessment of plasticizer compatibility in the polymeric composition under compression.

Mass loss (retained) after oven-aging, expressed as a percentage of the unaged mass, was determined on specimens of 37 mm diameter and 0.8–1.0 mm thickness. Visual observations of the surface were made to check for exudate (spew), as a measure of plasticizer compatibility under thermal stress.

Tensile strength (stress at break, which happened to be equal to peak stress and yield stress) and tensile elongation (strain at break) of unaged as well as oven-aged samples were measured according to ASTM D638 and UL 1581/2556, at a displacement rate of 51 mm per minute (using Type IV dog bone-shaped specimens of 0.8–1.0 mm thickness). The averages of three to five measurements at each condition were determined. Tensile strength retained (TSR) as well as tensile elongation retained (TER) were computed as percentages of the unaged values.

## RESULTS AND DISCUSSION

The thermogravimetry characteristics of the individual plasticizers are shown in Figure 1(a). The most volatile plasticizer was e-FAME, and the least volatile was ESO. FDAE-1 and FDAE-2 were close in volatilities to the phthalates, while the thermogravimetry of FDAE-3 was similar to that of TOTM. Differential thermogravimetry (not plotted herein) showed only one peak each with the phthalates, trimellitate and all three FDAE materials. This indicates that all of these materials were largely comprised of single chemical structures. In contrast, the epoxidized derivatives (ESO and e-FAME) exhibited multiple peaks, signifying that they were constituted of different fractions—likely



**Figure 1.** Effect of plasticizer molecular weight on: (a) thermogravimetry of plasticizer; and (b) hardness of plasticized PVC.

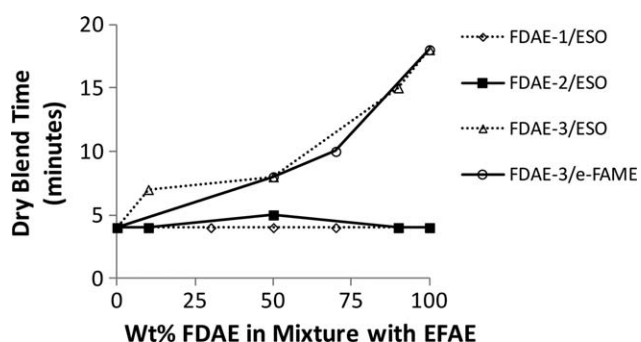
arising from the varied fatty acid composition of the starting triglyceride.<sup>23</sup>

When making the dry blends, with the exception of FDAE-3, all other individual plasticizers were completely absorbed in the porous PVC within 5 min at a set temperature of 90°C, well above the 83°C glass transition temperature of the polymer,<sup>10</sup> although there were some differences in absorption times. The trimellitate was slower to absorb than the phthalates, consistent with previous findings,<sup>11</sup> due to its comparatively higher molecular weight. Interestingly, the uptakes in the polymer of ESO (of highest molecular weight) and e-FAME (of lowest molecular weight) occurred relatively quickly, with absorption times similar to those reported previously for ESO.<sup>11</sup> In sharp contrast, the dry blend time observed with FDAE-3 was 18 min (much greater than that of TOTM of similar molecular weight). These findings were in agreement with the results of another study which showed that, in addition to molecular weight, functional groups of plasticizers can also influence absorption times significantly,<sup>11</sup> possibly due to variations in hydrophilic–lipophilic balance or solubility parameters. Within the family of FDAE materials, the significantly longer dry blend times observed with FDAE-3 can in part be attributed to its relatively high molecular weight. Mixing increasing amounts of EFAE (either ESO or e-FAME) with FDAE-3 led to faster plasticizer absorption, but did not have appreciable effects with the other FDAE materials (Figure 2).

There was a reasonable correlation of the two different hardness measurements made on specimens that were compression

molded from the various dry blends: Shore A = 0.84(Shore D) + 60.47;  $R^2 = 0.94$ . The unaged values of tensile strength ranged from 17 MPa to 24 MPa (tending to increase with increasing hardness) and tensile elongations ranged from 286% to 354%, with e-FAME as single plasticizer yielding the lowest tensile strength and greatest tensile elongation. Plasticization efficiencies were inferred from hardness measurements, since the hardness of a material is reflective of its flexibility and the plasticizers were all used at equivalent loadings. Tensile properties were not used to assess plasticization efficiencies, as the effects of plasticizer types on unaged values of tensile strength and elongation were less pronounced than those on hardness. The hardness and tensile measurements, along with their standard deviations, are also provided in tabular form as Supporting Information (Table S1). Apart from ESO, there was a trend of lower plasticizer molecular weight resulting in greater plasticization efficiency [Figure 1(b)]. In percentage terms, there was greater differentiation of the Shore D measurements than of the Shore A results. Compared with DEHP and DIDP, the FDAE-1 and FDAE-2 materials tended to yield lower values of Shore D hardness. In contrast, FDAE-3 led to a relatively hard composition (9% greater Shore D than that attained with TOTM, for instance). Especially impressive was the observation that ESO led to 8% lower Shore D than TOTM, even though its molecular weight was almost twice that of the latter. Since e-FAME followed the same trend as the phthalates and FDAE materials (yielding 26% lower Shore D than DEHP by virtue of the lower molecular weight of e-FAME), it is not just the epoxy groups in ESO that can account for its remarkable plasticization efficiency. Increasing proportions of ESO in mixtures with FDAE-1 or FDAE-2 tended to yield harder compositions, whereas replacing even a minor proportion of FDAE-3 with ESO or e-FAME decreased hardness measurably (Figure 3). Of the epoxidized bioplasticizers, the lower molecular weight derivative (i.e., e-FAME) was substantially more effective at plasticizing the polymer—either as a single plasticizer or in mixtures with FDAE-3.

In wire and cable applications of plasticized PVC, important considerations are the retentions of tensile strength and tensile elongation upon aging at elevated temperatures. In the case of compositions plasticized with DEHP, DIDP, and TOTM, the percentage values of tensile strength retained (TSR) after 7 days of aging at 100°C/113°C/136°C were 116/276/283, 98/92/186, and 89/88/92, respectively. The corresponding percentage values of tensile elongation retained (TER) for these systems were as



**Figure 2.** Dry blend times of FDAE/EFAE plasticized PVC compositions.

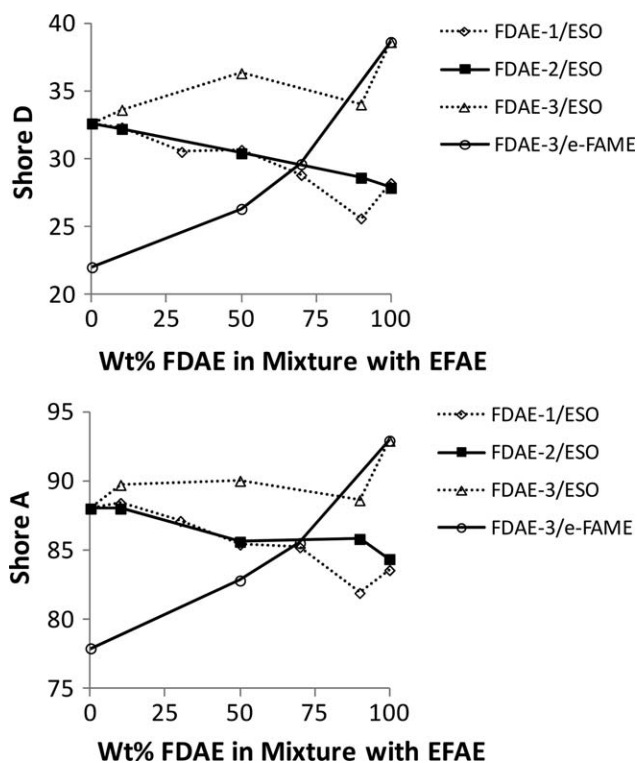


Figure 3. Hardness of FDAE/EFAE plasticized PVC compositions.

follows: 10/2/1, 98/80/1, and 95/88/82, respectively. At the highest temperature of 136°C, the values of mass retained were 70%, 75%, and 97% (with DEHP, DIDP, and TOTM, respectively). For FDAE/EFAE plasticized compositions, the heat aging tensile data are presented in Figures 4–7 and mass loss characteristics at a temperature of 136°C are shown in Figure 8 (with more comprehensive findings presented in Table S1 of the Supporting Information). The molecular weights (and associated temperatures for mass losses by thermogravimetry) of the plasticizers were observed to be key determinants of the thermal aging characteristics of the plasticized polymer, but not the only factors. Usually (but not always), the more volatile plasticizers yielded greater mass losses of the plasticized compositions upon heat aging and in most (but not all cases) inferior retentions of tensile properties. Rather surprisingly, in the case of FDAE-3 based compositions, the substitution of minor proportions of this plasticizer with ESO or e-FAME led to significantly better mass retention at 136°C in the case of the former and no change with the latter (Figure 8). This observation, together with the correspondingly decreased hardness mentioned earlier, was indicative of significant enhancements in the plasticizer–polymer interactions through the addition of either EFAE to FDAE-3. In terms of TER, neither FDAE-1 nor DEHP performed well even at the lowest temperature of 100°C, but e-FAME surprisingly yielded a high value at this temperature (in spite of it being of greater volatility than these two). This effect might be attributed to the stabilizing effect of e-FAME, since epoxy compounds are known to stabilize PVC by reacting with any hydrogen chloride liberated from the polymer.<sup>24</sup> FDAE-2 and DIDP yielded acceptably high values of TER up to a temperature of 113°C. The best heat aging characteristics

(with single plasticizers) were observed with FDAE-3, ESO and TOTM (i.e., sufficiently high values of TER at temperatures as high as 136°C). Of the epoxidized plasticizers, e-FAME yielded poorer heat aging behavior than ESO. Increasing amounts of ESO in mixtures with the FDAE-1 and FDAE-2 materials often led to improved heat aging performance (Figures 4 and 5). No pronounced effects on TER were evident with FDAE-3/ESO mixtures (Figure 6), but increasing proportions of e-FAME in mixtures with FDAE-3 tended to have deleterious effects (Figure 7). The effect of plasticizer mixture compositions on TER was not necessarily linear, with particularly rapid changes in TER often occurring when the proportions of EFAE generally exceeded 50 wt % (in the case of FDAE-1/ESO mixtures at all temperatures; FDAE-2/ESO mixtures at 136°C; and FDAE-3/e-FAME mixtures at 113°C and 136°C).

Figure 9 depicts the balance of heat aging performance at 136°C versus plasticization efficiency, comparing the effects of various plasticizer compositions. The proportions of ESO or e-FAME in combination with the FDAE materials ranged from 0 to 100 wt % (the exact compositions for the various data points can be identified by cross-referencing with Figures 3–7). e-FAME, FDAE-1, and FDAE-2 resulted in similarly poor TER values at 136°C as DEHP and DIDP, but at correspondingly greater plasticization efficiencies. On the other hand, ESO and some of the FDAE/ESO or FDAE/e-FAME mixtures yielded similar heat aging characteristics at 136°C as TOTM (i.e., TER of ~75% or greater), but at relatively greater plasticization efficiencies. Particularly noteworthy was the improved balance of plasticization efficiency and TER observed with 30–50 wt % of e-FAME in mixtures with FDAE-3. That is, plasticizers comprising FDAE,

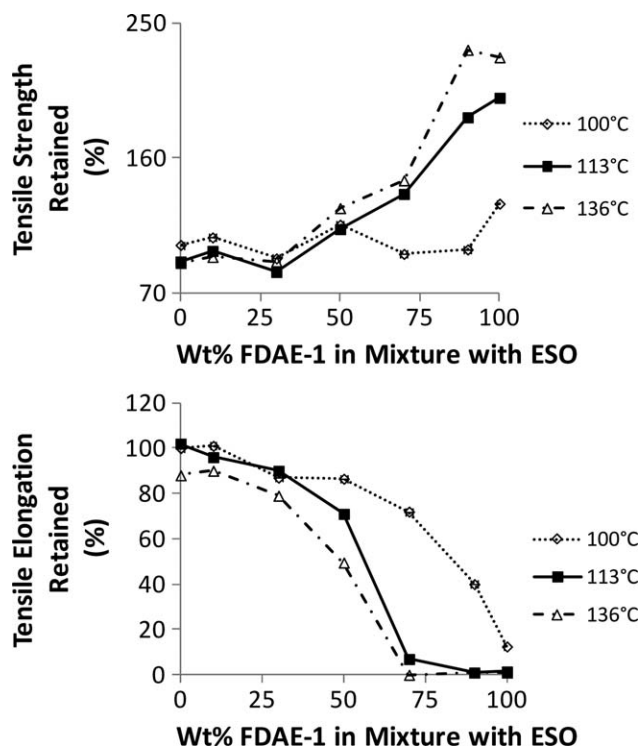
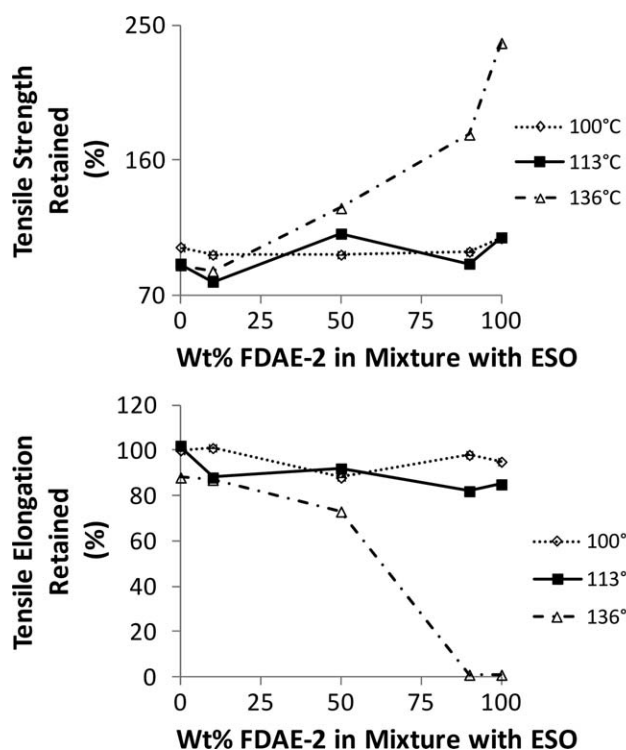
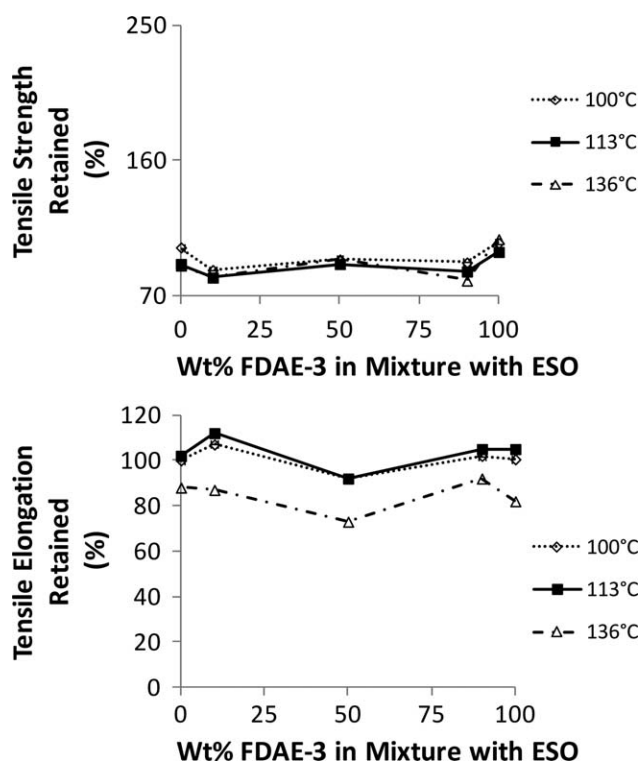


Figure 4. Changes in tensile properties of FDAE-1/ESO plasticized compositions after heat aging for 7 days.

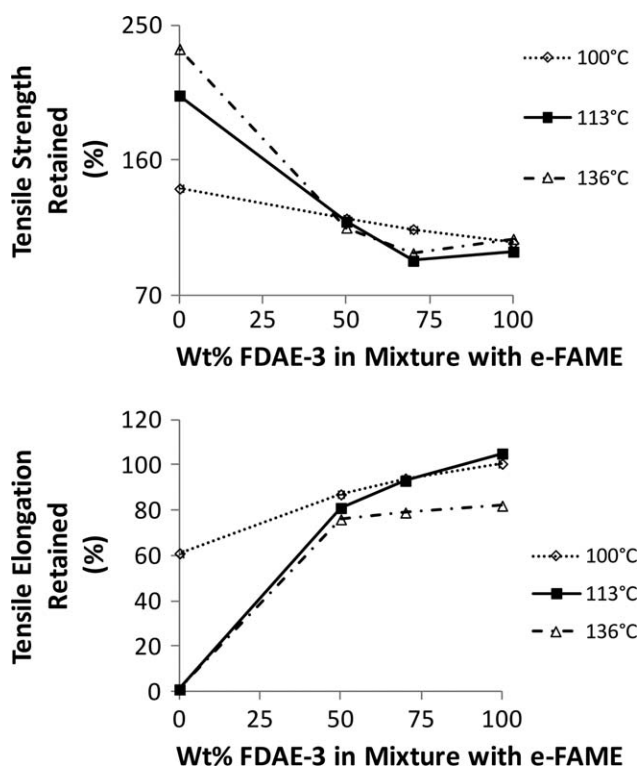


**Figure 5.** Changes in tensile properties of FDAE-2/ESO plasticized compositions after heat aging for 7 days.

EFAE, and/or FDAE/EFAE mixtures generally yielded better balance of hardness and TER of plasticized PVC than the phthalates and trimellitate.



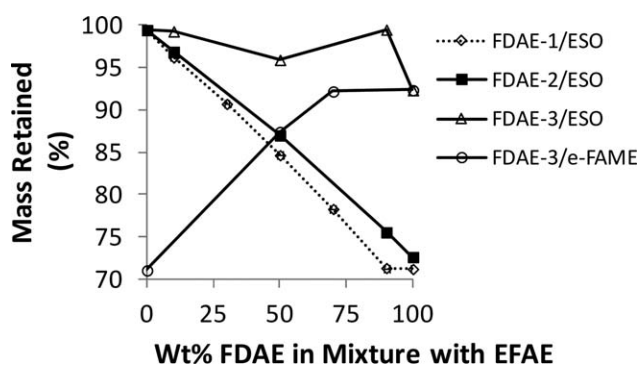
**Figure 6.** Changes in tensile properties of FDAE-3/ESO plasticized compositions after heat aging for 7 days.



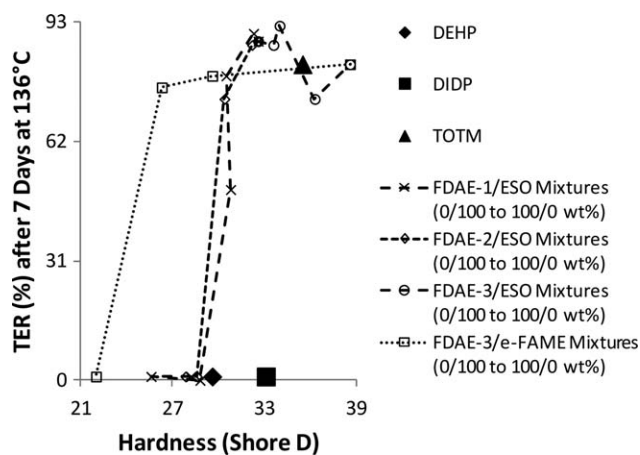
**Figure 7.** Changes in tensile properties of FDAE-3/e-FAME plasticized compositions after heat aging for 7 days.

Compatibility assessments of the plasticized polymer compositions under mechanical stress (i.e., loop spew) and thermal stress (i.e., from heat aging) revealed that the FDAE and EFAE materials, along with their mixtures, were generally compatible with PVC (as the specimens exhibited little or no evidence of exudation at the surface). Note that the type of heat stabilizer used herein has been demonstrated to be very effective at stabilizing PVC compositions comprising EFAE as plasticizers or coplasticizers,<sup>14</sup> as have been some other heat stabilizers.<sup>15,16</sup>

The results of this study on FDAE, EFAE and their mixtures as PVC plasticizers can also be compared with those from a previous investigation of bis(2-ethylhexyl) succinate and its mixtures with ESO, with similar types and proportions of the other



**Figure 8.** Mass retentions of FDAE/EFAE plasticized compositions after aging for 7 days at 136°C.



**Figure 9.** Heat aging performances versus plasticization efficiencies obtained with different plasticizer compositions.

ingredients in the formulations.<sup>11</sup> Although the FDAE materials were not as effective as the succinate at plasticizing PVC (decreasing Shore D), because of their relatively higher molecular weights, they generally yielded better heat aging characteristics (especially in mixtures with ESO or e-FAME). The succinate was also inferior to e-FAME as a single plasticizer in terms of plasticization efficiency and tensile elongation retention upon aging at 100°C.

## CONCLUSIONS

The volatilities of the plasticizers were largely dependent on their molecular weights, not their different chemical structures, with e-FAME being the most volatile and ESO the least volatile. PVC plasticization efficiency generally also varied with the molecular weight of the plasticizer, with ESO being a particularly notable exception (in that it was much more effective at softening the polymer than anticipated from its relatively high molecular weight).

FDAE, EFAE, and mixtures thereof were found to be sufficiently compatible and effective plasticizers for PVC, exhibiting varying degrees of interactions with the polymer and generally yielding better balance of plasticization efficiency and thermal aging performance than the phthalates or trimellitate. The composition plasticized with ESO performed satisfactorily at aging temperatures up to 136°C, while that made with e-FAME did remarkably well at a temperature of 100°C in comparison with FDAE-1 and DEHP of higher molecular weight (likely due to the additional function of e-FAME as acid scavenger). Especially excellent balance of hardness and heat aging characteristics was obtained with FDAE-3/e-FAME mixtures comprising 30–50 wt % e-FAME.

These findings demonstrate that FDAE of a range of molecular weights, as well as their combinations with EFAE (either e-FAME or ESO), can be sustainable PVC plasticizers for meeting the demanding heat aging requirements of wire and cable applications, while at the same time delivering improved plasticization efficiencies.

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