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TESTING

Material Properties

Nontoxic bio-plasticizers for PVC as replacements for conventional toxic plasticizers

Witold Brostow*, Xinyao Lu, Allison T. Osmanson

Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North, Texas, 3940 North Elm Street, Denton, TX, 76207, USA



ARTICLE INFO

Keywords:

PVC plasticizers
Plasticizer toxicity
Hydrogenated castor oil
Epoxidized soybean oil

ABSTRACT

Stretched PVC film samples were created to compare the performance of toxic and non-toxic plasticizers. The reference films were produced with dodecyl phthalate and trinonyl benzene-1,2,4-tricarboxylate. Comparable films were created using non-toxic plasticizers, hydrogenated castor oil, epoxidized soybean oil, and a mixture of both. The hydrogenated castor oil is a mixture of glycerin acetates and acetic acid esters of mono- and diglycerides of fatty acids while epoxidized soybean oil is a plasticizer employed in toy and childcare applications. Plasticizer migration, tensile properties and dynamic friction were determined and compared. The combination of hydrogenated castor oil and epoxidized soybean oil based plasticizers shows comparable mechanical performance of that PVC to PVC with conventional toxic plasticizers.

1. Introduction

Poly (vinyl chloride) (PVC) is applied in a variety of industries, including biomedical, toy manufacturing, food packaging, construction, and cable and wire manufacturing. The advantages include low cost and high versatility [1–3]. However, pure PVC is a rigid polymer while many industries require PVC to have flexibility and processability [4]. In order to improve those two properties, PVC is often blended with plasticizers [5]. Unfortunately, often there is migration of plasticizers to the surface [6–8], resulting in very soft, sticky, and fragmented PVC products. Studies have shown that plasticizers containing a benzene ring would result in low migration rates. The most common plasticizers used in industrial scale are based on phthalates, such as dioctyl phthalate (DOP), dodecyl phthalate (DTP), dibutyl phthalate (DBP) and trinonyl benzene-1,2,4-tricarboxylate (TINTM) [9,10]. However, DTP and TINTM plasticizers are severely toxic. Plasticizers of the phthalate family have been studied from the point of view of their negative effects on infant nutrition and reproductive health [11] while there is increasing interest in low environmental effect plasticizers [12]. Bio-based plasticizers are environmentally appealing - also because they are extracted from renewable resources. Such resources include sunflower oil, castor bean oil, and flaxseed oil, to name a few [13]. Bio-based plasticizers could be useful for applications that are especially sensitive to migration and subsequent toxicity, such as the wire and cable manufacturing industry, food packaging and children toys [14].

Certain plasticizers such as those fully acetylated mono glyceride

based on hydrogenated castor oil (SNS), derived from 12-hydroxystearic castor oil, glycerin and acetic acid with viscosity 106 cPs have been approved by the European Union for food contact use without any restrictions.

Another vegetable based plasticizer is epoxidized soybean oil (ESBO), a kind of renewable oil with viscosity 35 cPs; it has been long known as secondary plasticizer and a secondary stabilizer in PVC. ESBO is available with iodine value as low as 1 g I₂/100 g, i.e. ≈ 0.04 mol double bonds in each molecule of ESBO. We anticipate that these plasticizers will prove to be more compatible with PVC. Epoxidized vegetable oils have been used as stabilizers [15,16].

The aim of this study was to compare the performance of non-toxic plasticizers such as SNS and ESBO with conventional toxic ones when used with PVC films. The main application is for the wire and cable manufacturing industry. During wire installation the dynamic friction is important, hence values of that friction are included also.

2. Experimental

2.1. Materials

PVC resin provided by Encore Wire Corp. was SNS, offered by Danisco, derived from 12-hydroxystearic castor oil, glycerin and acetic acid with viscosity 106 cPs, density 1.104 g/cm³ and saponification value 435 at room temperature. Saponification is the number of milligrams of potassium hydroxide required for the complete neutralization

* Corresponding author.

E-mail addresses: wkbrostow@gmail.com (W. Brostow), xinaolu@my.unt.edu (X. Lu), allison.osmanson@gmail.com (A.T. Osmanson).

(“saponification”) acids present in 1 g of substance. The name saponification comes from the fact that this process is applied in soap manufacture. ESBO (Olvex 51), from SGS Polimeros is a renewable soybean oil with viscosity 35 cPs, density 0.98 g/cm³ at room temperature and flash point = 225 °C. DTDP also from Encore Wire Corp. is ditriglyceride phthalate C₃₄H₅₈O₄ with molecular weight 530.8, density 0.96 g/cm³, viscosity 190 cP at room temperature and flash point = 242 °C. TNTM is trinonyl benzene-1,2,4-tricarboxylate, also from Encore Wire Corp. Thermal stabilizers provided by Encore Wire Corp. are the same in all samples.

2.2. Film preparation

Stretch PVC films with different plasticizer compositions were produced for this study at Encore Wire Corp. in an extruder. The plasticizer compositions are as follows:

Sample 1: PVC + 20 wt% DTDP + 30 wt% TIMTM + thermal stabilizer + additives (control);

Sample 2: PVC + 50 wt% SNS + thermal stabilizer + additives;

Sample 3: PVC + 50 wt% ESBO + thermal stabilizer + additives;

Sample 4: PVC + 25 wt% SNS + 25 wt% ESBO + thermal stabilizer + additives.

Sample 1 was adopted as reference to compare performance in terms of tensile properties of the stretched PVC films. Each group of samples consisted of 40 specimens. We have also determined water absorption and dynamic friction. Tests were conducted at 23 °C ± 2 °C and 50% ± 5% relative humidity after conditioning the samples in these same conditions for at least 48 h.

2.3. Exudation analyses

Exudation of the plasticizer was evaluated by placing a sample of film vertically in a drying oven under varying temperatures for 168 h. After this period, the weight increment of the film was determined and the extent of plasticizer exudation was calculated. All four groups of samples were weighed at room temperature and then put into oven at 80 °C, 100 °C, 121 °C, and 136 °C for 168 h. At least five specimens at each temperature have been evaluated - as in a study by Marin and coworkers [10].

2.4. Tensile properties

Mechanical properties tensile strength (TS), tensile elongation at break (ϵ_b) and Young's modulus (E) of the films were determined at room temperature using a Mariana Tensile (TestWorks[®]4, USA) machine according to ASTM D882 [17]. Some dog-bone shaped specimens were cut from flattened PVC sheets obtained from the extruder. The dimensions of the dog-bone specimen are consistent with ASTM D638 type IV [18]. Eight specimens were tested for each kind of sample at 5.0 mm/min tensile speed using a MTS[®] QTEST/5 Universal Testing Machine.

2.5. Migration stability tests

Migration of the plasticizers from film samples was carried out in water at 90 °C. Samples were weighed and sealed in beakers of 100 mL

of water. They were then placed in an oven at 90 °C. The systems were removed after 15 min, 30 min, 1 h, 3 h, 6 h, 12 h, 24 h, 48 h, 3 days, 4 days, 5 days, 6 days and 7 days. All samples were dried and weighted after each allotted period. The percentage of mass loss was calculated in relation to the initial plasticizer mass added to the sample. The average weight changes of three specimens of each sample were recorded until no obvious weight increments were observed. The weight change can be simply calculated as:

$$\text{Weight change} = (W - W_i)/W_i \times 100\% \quad (1)$$

where W and W_i represent the current weight and the initial weight of a specimen. Typically, all specimens stopped absorbing water on the seventh day of tests - as in an earlier study [19].

2.6. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out in a thermogravimetric analyzer (Magnetic Calibration Standards Kit 2109-0071, PerkinElmer, USA) in a N₂ atmosphere (50 mL/min, purity 99.8%). Samples were heated from 25 °C to 800 °C at a heating rate of 20 °C/min, maintaining 800 °C for 1 min and then cooling down.

2.7. Dynamic friction analysis

Tribology is a very broad area that includes the studies of friction, lubrication, wear, adhesion, scratch resistance and any interactions of multiple surfaces; it is related via brittleness to mechanical properties [20–22]. Dynamic friction is important for the present applications and has been determined by using a tribological tester from Nanovea Inc. in the “pin-on-disk” mode. As the name implies, a specimen is secured on a spinning disk and it is contacted with a stationary pin which is subjected to normally 5.0 N forces while the machine is running. A SS302 stainless steel ball with 3.2 mm diameter is used as a pin in this work. During the testing, the total sliding distance is 75.36 m (6000 revolutions and a track with 2 mm radius) and the spinning speed is 200 revs/min.

2.8. Morphology of film surfaces (SEM)

Samples tested under different temperatures were observed in SEM (TM3030 Plus Tabletop Microscope from Copyright[®] Hitachi High-technologies Corporation 2014).

3. Results and discussion

3.1. Exudation analysis results

Plasticized PVC (with a natural plasticizer additive) films produced by extrusion show a yellowish and homogenous surface. The average thicknesses of plasticized PVC films are listed in Table 1. The chemical modification of the natural plasticizer does not show a significant influence in film thickness compared to the other plasticized PVC matrices.

Fig. 1 shows the remaining weight percentages of PVC samples with all plasticizers. As the temperature increases, however, DTDP + TINTM plasticizers weight retention remains over 98% because of the benzene rings resistance to migration.

We see in Fig. 1 that the amount of weight loss increases with

Table 1
Thickness of all PVC components.

Component	PVC + DTDP + TINTM	PVC + ESBO	PVC + SNS	PVC + ESBO + SNS
Thickness (mm)	1 ± 0.09	1 ± 0.1	1 ± 0.07	1 ± 0.11

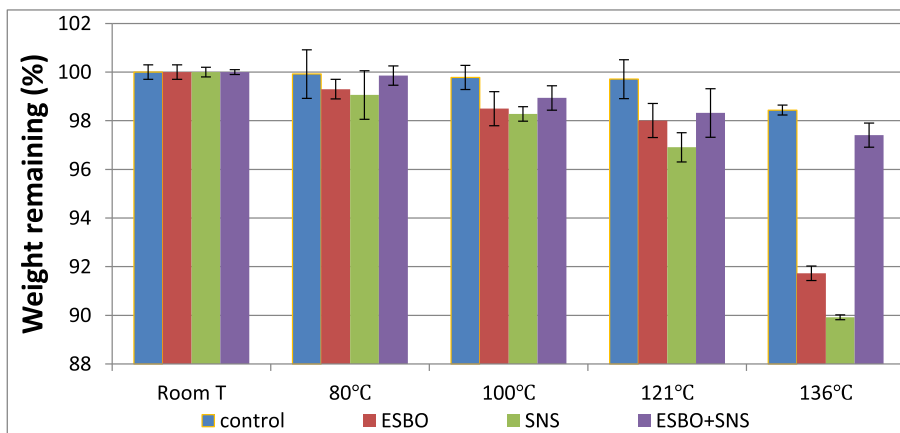


Fig. 1. Exudation results for 4 kinds of samples at several temperatures.

increasing temperature—as expected. The differences between PVC samples with DTDP + TINTM (control) and ESBO + SNS are not large; the latter is lower than the former by about 1.39% at 121 °C and 1.04% at 136 °C. Thus, while migration stability in the presence of either SNS or ESBO is not high, the combination of SNS with ESBO provides migration stability comparable to that of PVC films with DTDP + TINTM plasticizers.

3.2. Tensile testing results

Tensile testing results are displayed in Figs. 2–4. All samples became stiff as they were exposed to increasing temperatures, and plasticizers of all samples had seepage at temperatures higher than 121 °C. The oil-like plasticizer seeping into the surface was accompanied by concomitant modulus increase. The highest tensile Young moduli are seen at 136 °C. The E values of PVC with SNS + ESBO are relatively more stable against temperature changes than those of SNS and ESBO mixed individually with PVC. The ESBO + SNS mixture has even slightly higher tensile toughness than the control sample.

As for elongations at break, we are dealing with two opposite effects. On one hand, the increase of temperature causes a loss of the plasticizer, hence a lower ϵ_b . On the other hand, an increase in T causes an increase of the free volume in polymers [23]. The change of the plasticizer content in the films with temperature is irregular – a fact reflected in maxima and minima of ϵ_b values for a given composition as

a function of temperature. Pertinent for our application is the fact that ϵ_b values at 136 °C for the composites with either ESBO or SNS are negligible, hence such films exposed to high temperatures are useless for our purposes. At the same time, we see a synergy between SNS and ESBO for elongations at break at 136 °C. An explanation of this is likely to involve the strength of the interactions between the hydroxyl groups in SNS and epoxy rings in the ESBO.

The stress-strain curves show how ESBO sample and SNS samples cracked at 136 °C and 121 °C, respectively.

3.3. Water absorption tests results

Figs. 5–9 display these results for several temperatures as percentage weight increases.

There is a clear pattern seen in the above series of figures. After 7 days, the weight increases of all other samples are significantly higher than for the control sample – except for ESBO at 121 °C which behaves very similarly to the control. Possibly the two opposite effects noted above in Section 3.2 are involved. Apparently our new bio-based bio-plasticizers lack the benzene rings which enhance the migration resistance because those rings are relatively large and flat, hence resistant to displacement. As the temperature increases, the weight of PVC with bio-based plasticizers increases significantly – without much differences between SNS, ESBO and SNS + ESBO plasticizers. This while the weight increase in TINTM + DTDP-containing PVC is not as significant as the exudation temperature increases.

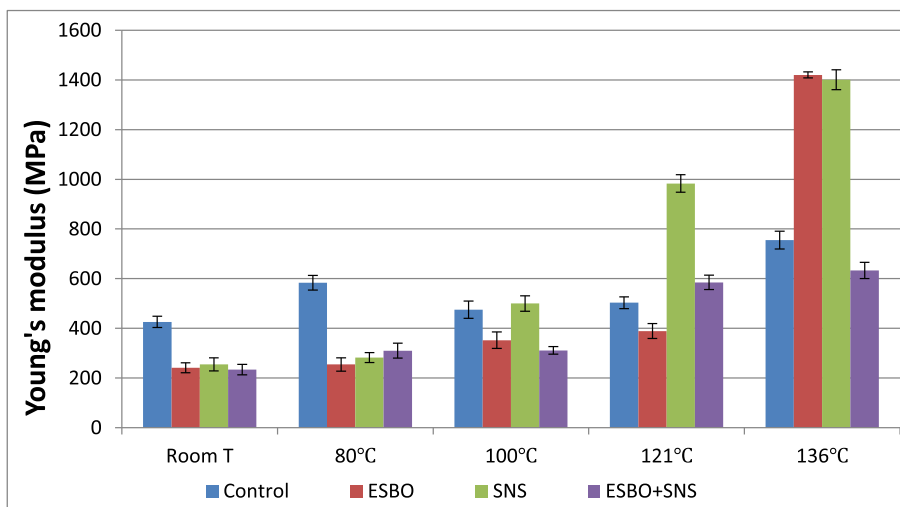


Fig. 2. Young's moduli.

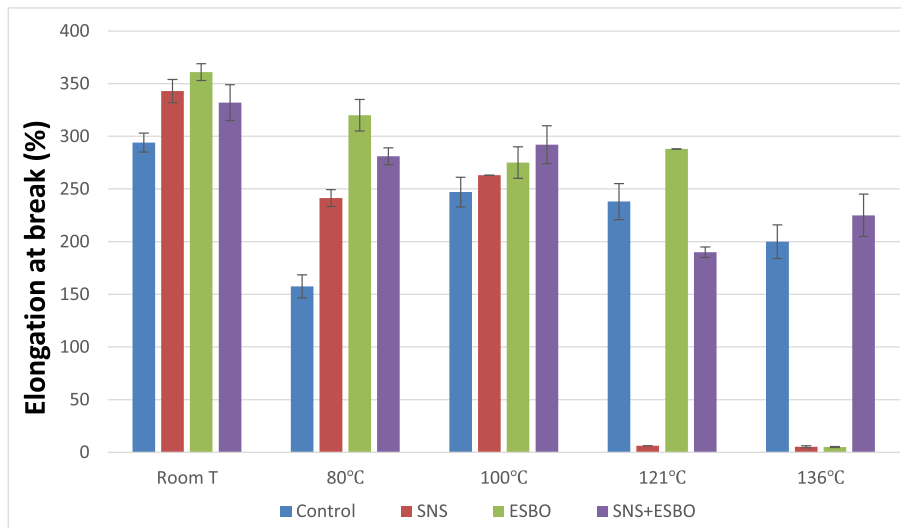


Fig. 3. Elongations at break.

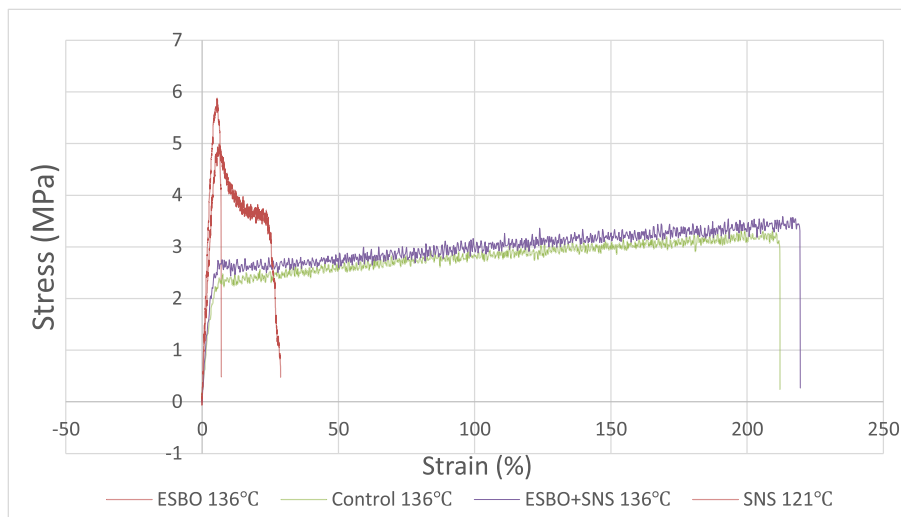


Fig. 4. Stress vs. strain diagrams.

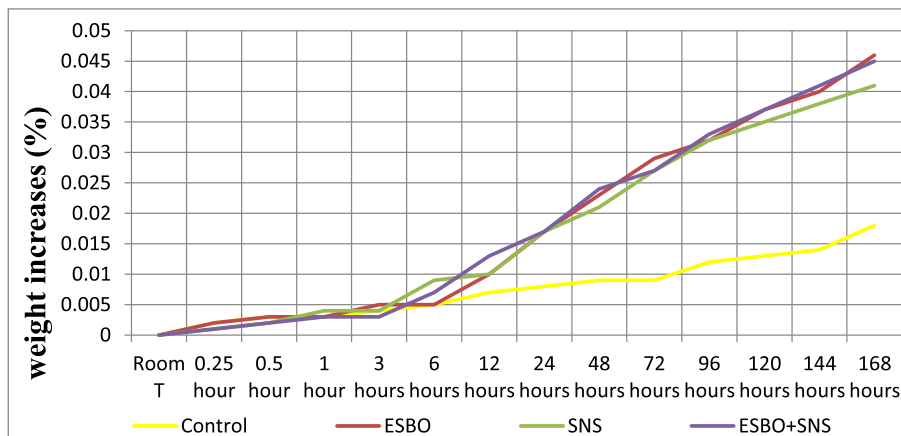


Fig. 5. Water absorption at room temperature.

3.4. Dynamic friction results

Fig. 10 shows the dynamic friction values.

In general, the dynamic friction values do not show dramatic

differences - while some nuances can be found. At room temperature, the dynamic friction of PVC with ESBO + SNS and DTDP + TINTM samples are lower than those of the ESBO and SNS containing samples by some 25%. After high-temperature exposure, however, the

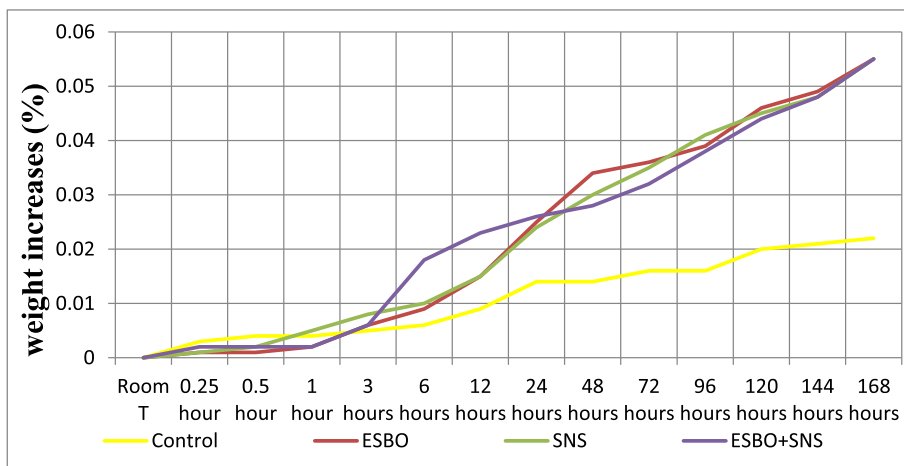


Fig. 6. Water absorption at 80 °C.

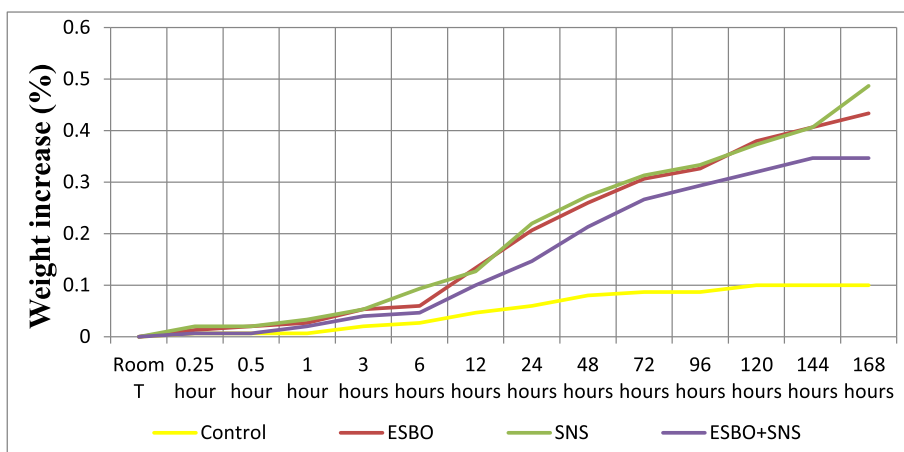


Fig. 7. Water absorption at 100 °C.

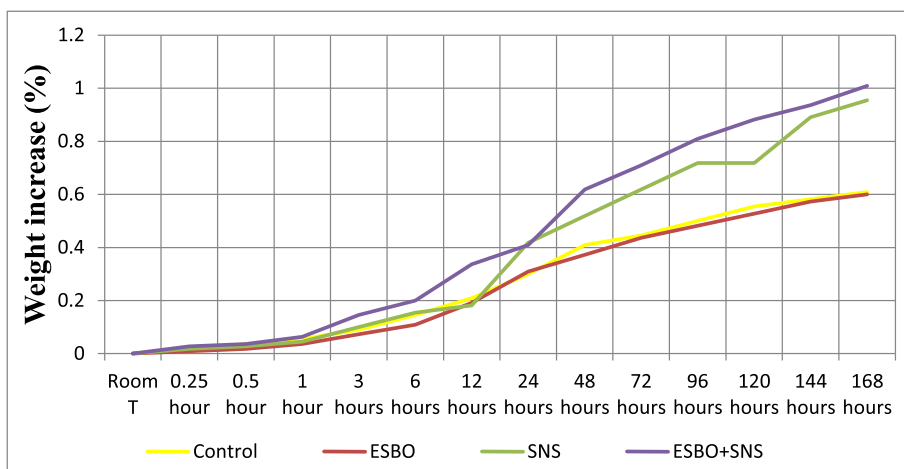


Fig. 8. Water absorption at 121 °C.

differences between the friction values of different compositions are not significant.

3.5. Thermogravimetric analysis (TGA) results

Fig. 11 shows weight loss curves of ESBO + SNS and DTDP + TINTM samples after being subjected to 136 °C exposure.

The first descent seen in Fig. 11 reflects the de-chlorination of PVC,

the main component, with the formation of HCl. The second descent is attributed to polymer crosslinking including C-C bonds. As seen in the Figure, the decomposition of both materials begins around 300 °C. From the point of view of thermal stability, the differences between the two materials are not significant.

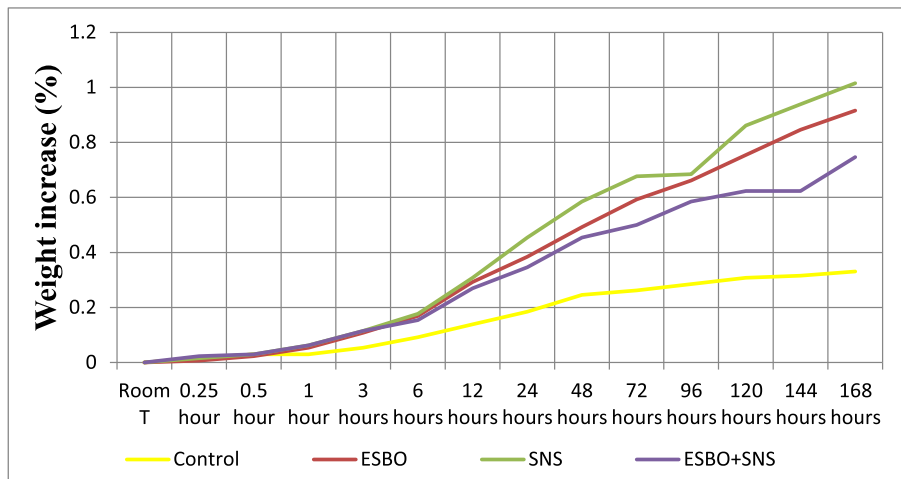


Fig. 9. Water absorption at 136 °C.

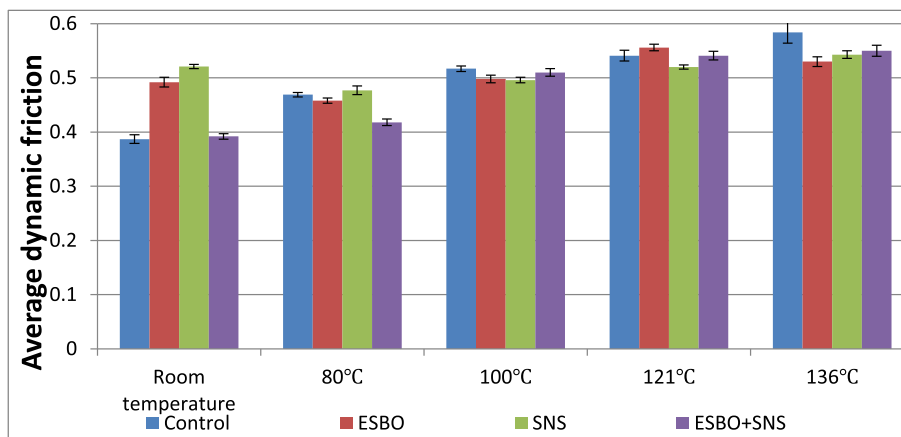


Fig. 10. Dynamic friction results for PVC with plasticizers.

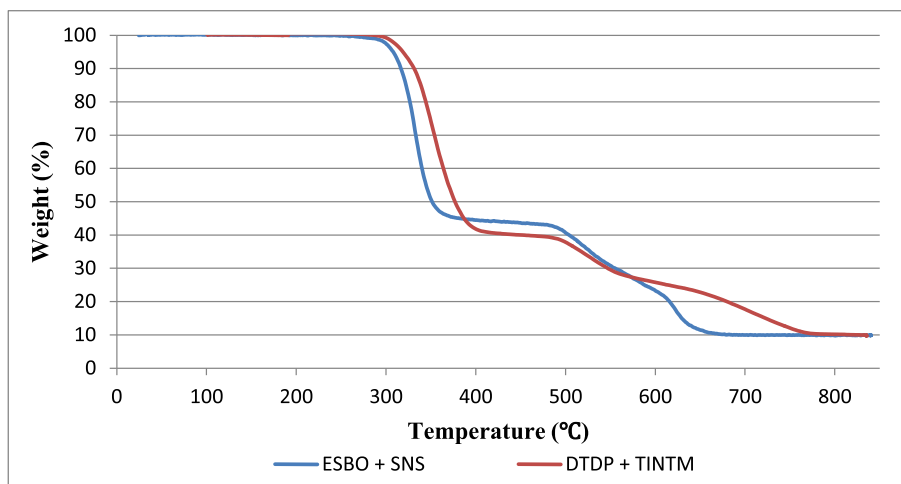


Fig. 11. TGA results of PVC samples with two types of plasticizers after heating to 136 °C.

3.6. Morphologies of film surfaces (SEM)

Selected fracture surfaces are shown in Figs. 12–14.

The fracture surfaces of all PVC films are neat without filaments; almost all fracture points are in the middle of dogbone shaped samples. Surfaces of unheated samples (not shown here for brevity) are uniform and gray in color. After exposure to higher temperatures, some dark

spots appear. Further temperature increases cause increases in the numbers of dark spots. PVC films with DTDP + TINTM and with SNS + ESBO show relatively fewer dark spots when compared to SNS or ESBO plasticized samples. This agrees with the results reported in Section 3.2, in Fig. 4 in particular. We see in that Figure for 136 °C that the curves for the control and for ESBO show much shorter elongations at break than for the SNS + ESBO. We recall that the elongation at

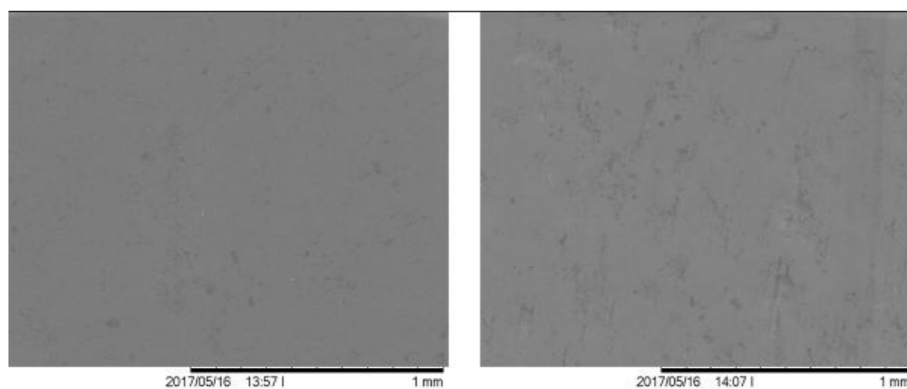


Fig. 12. SEM surfaces of PVC components with SNS plasticizer after exposure to 100 °C (left) and 121 °C(right).

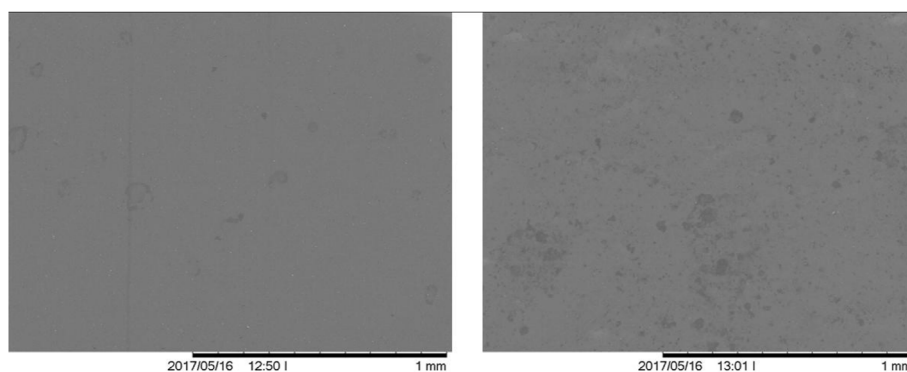


Fig. 13. SEM surfaces of PVC components with ESBO plasticizer after exposure to 121 °C (left) and 136 °C(right).

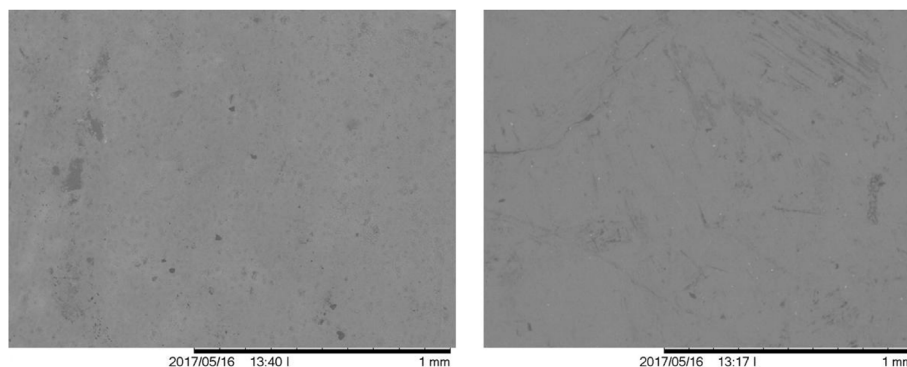


Fig. 14. SEM surfaces of PVC films with DTDP + TINTM plasticizer after exposure to 136 °C (lef) and with SNS + ESBO plasticizers after exposure to the same temperature (right).

break is inversely proportional to brittleness B [22]. Apparently B manifests itself also in the dark spots seen for SNS or ESBO plasticized samples.

4. Concluding remarks

Although traditional DTDP + TINTM plasticized PVC films have somewhat better properties, new types of bio-plasticizer are promising. While ESBO and SNS plasticizers individually do not show that well desired properties compared to DTDP + TINTM plasticizers, the combination of ESBO and SNS provides properties comparable to DTDP + TINTM plasticizers. Thus, replacing traditional toxic plasticizers with bio-based and non-toxic ones is doable.

Some of the conclusions reached in our work are only confirmations of earlier results of Ekelund, Edin and Gedde [14] who have also studied plasticized PVC for cable insulation. This pertains among others to

an increase of tensile modulus and a decrease of strain at break as a consequence of the loss of plasticizer by migration.

PVC is used in various combinations, often as a matrix with a variety of fillers such as clay [24], nano- CaCO_3 [25] or montmorillonite [26], hence the problems of PVC aging appear there as well. Finally, let us note that plasticized PVC is also used in preservation of heritage collections. Thus, Adeline Royaux and her colleagues studied effects of PVC aging from this point of view [27].

Acknowledgments

Partial support of this work by Encore Wire Corp. is gratefully acknowledged. Constructive comments of the editor and reviewers helped to improve the perspicuity of this paper.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymertesting.2018.03.007>.

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