

Absorption and migration of bio-based epoxidized soybean oil and its mixtures with tri(2-ethylhexyl) trimellitate in poly(vinylchloride)

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ABSTRACT: The efficacy of epoxidized soybean oil (ESO), tri(2-ethylhexyl) trimellitate, and mixtures thereof as plasticizers for poly(vinylchloride) has been studied. At 80°C, the trimellitate was slower to absorb in this polymer than ESO and was also less soluble, but the former exhibited higher solubility at 120°C. Plasticization efficiencies of stabilized polymeric compositions were similar with ESO and the trimellitate (despite their very different molecular weights). The trimellitate yielded greater mass loss during heat aging of the plasticized compositions, but substituting even minor amounts of it with ESO decreased mass loss synergistically. The trimellitate also resulted in more of an increase in hardness than ESO over time at elevated temperatures, but when aged at 120°C, mixtures of the two surprisingly had more deleterious effects. Thus, although ESO can replace part or all of trimellitates in plasticized PVC, using it as sole plasticizer would be preferable when heat aging performance is a requirement. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41966.

KEYWORDS: biomaterials; plasticizer; poly(vinyl chloride)

Received 2 October 2014; accepted 24 December 2014

DOI: 10.1002/app.41966

INTRODUCTION

Tri(2-ethylhexyl) trimellitate, also known as trioctyl trimellitate (TOTM), is often used to plasticize poly(vinylchloride) (PVC),^{1–7} either by itself or in mixtures with phthalate plasticizers. However, there is growing interest to substitute part or all these petroleum-derived plasticizers with more sustainable bio-based materials that are derived from renewable resources.^{8–14} A comparatively inexpensive bioplasticizer is epoxidized soybean oil (ESO), which has generally been used as a secondary plasticizer and co-stabilizer for PVC, but more recently has also been contemplated as a primary plasticizer for PVC.^{15–19} Important considerations in plasticizer selection include their solubility and transport characteristics in the polymer.^{19–21} Mixtures of ESO with bio-derived *bis*(2-ethylhexyl) succinate have also been shown to be promising plasticizers for PVC.^{22,23}

This article describes the absorption and migration of TOTM and its mixtures with ESO in PVC, in comparison with that of ESO alone, which was reported earlier.¹⁹ Although TOTM and ESO have been studied before as individual plasticizers for this

polymer, there are very few direct comparisons of the two described in the literature and their mixtures have not previously been investigated. In particular, the comparative solubilities of TOTM, ESO, and their mixtures in PVC have not been assessed previously, nor have the effects of the mixtures on heat aging characteristics of plasticized PVC been described earlier. The results presented herein are significant because they portray the fundamental differences in solubility and transport characteristics of these plasticizers in PVC, and reveal some unexpected effects of the mixtures.

EXPERIMENTAL

Materials

The materials used were OxyVinyls 240F suspension-grade PVC homopolymer powder (product of OxyVinyls, LP; K-value of 70), Polyfil 70 calcined kaolin clay (as electrical insulation filler), Baeropan MC 9754 KA calcium-zinc mixed metal soap (as heat stabilizer), Irganox 1076 (as antioxidant), Tri(2-ethylhexyl) trimellitate (TOTM; as plasticizer or co-plasticizer; Eastman grade; product of Sigma-Aldrich; density

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at 25°C of 0.987 g/mL), and Plas-Chek 775 epoxidized soybean oil (ESO; as plasticizer or co-plasticizer). The ESO had an iodine value of 0.7 g I₂/100 g, oxirane oxygen content of 7.2%, density at 25°C of 0.993 g/mL and APHA color of 123.¹⁹

Plasticizer Uptake by Centrifuge Plasticizer Absorption Test

The determination of plasticizer absorption in PVC powder was conducted using the Centrifuge Plasticizer Absorption test, the details of which have been described elsewhere,^{6,19} at test temperatures ranging from 40°C to 120°C and absorption times up to 720 min. Plasticizer absorption was expressed as g/100 g of PVC powder. By subtracting the amount of plasticizer absorbed in the pores of the resin, the uptake of plasticizer in the matrix polymer was computed. Scanning electron microscopy was also conducted on the PVC powder before and after absorption of plasticizer using instrument model JSM-6360LV (JEOL Ltd. Japan).

Plasticizer Absorption by Torque Rheometer Test

Plasticizer uptake was also studied using a Haake Rheomix 600 p torque rheometer (Thermo Haake Company) equipped with twin-screw rotors (screw diameter: 16 mm; R/D of 25:1), using the procedure described previously¹⁹ and a composition comprising 68.2 wt % PVC, 29.2 wt % plasticizer (TOTM, ESO or TOTM/ESO mixtures), 2.3 wt % calcium-zinc metal soap, and 0.3 wt % antioxidant. Thus, the loading of plasticizer was 43 part-per-hundred resin (phr). Time-dependent changes in torque and composition temperature were recorded as the test was conducted at set metal temperatures of 80°C or 120°C and fixed revolutions per minute (30 rpm or 60 rpm).

Dry Blending, Melt Mixing, and Migration Testing of Flexible PVC Composition

The order of the various steps involved in the preparation and evaluation of the flexible PVC compositions was as follows: dry blending, melt blending, compression molding, specimen preparation, and property testing. Various samples of the following flexible PVC compositions were made: 63.9 wt % PVC, 27.3 wt % plasticizer (TOTM, ESO, or TOTM/ESO mixtures), 6.4 wt % calcined clay, 2.1 wt % calcium-zinc metal soap, and 0.3 wt % antioxidant. That is, the loading of plasticizer was 43 phr. Dry blends, melt blends and compression molded specimens were made and tested in accordance with the procedures described elsewhere.¹⁹ Migration testing of the plasticized (molded) specimens in contact with activated carbon was conducted at set temperatures of 40°C, 80°C, or 120°C for varying lengths of time to determine mass loss as a function of time. Additionally, the glass transition temperature (T_g) and hardness at 23°C (Shore D, average of six values, in accordance with ASTM D2240) were determined. The mass and hardness measurements were conducted after the specimens had been conditioned for 48 h at 23°C. The T_g was measured with Differential Scanning Calorimeter 204 HP Phoenix (Netzsch Analyzing & Testing) by conducting a temperature sweep from room temperature to 120°C at 5°C/min under air.

RESULTS AND DISCUSSION

The uptake of TOTM in PVC powder by the Centrifuge Plasticizer Absorption test, at various temperatures, is shown in Figure 1(a). As described previously,¹⁹ the amount of plasticizer

absorbed over a short duration at 40°C can be deemed to be a reasonable measure of the pore volume of the PVC resin, since the pericellular membrane surrounding the PVC granule does not impede uptake of plasticizer, due to pore openings in the topographical skin. After 10 and 20 min, these values were 28.1 and 28.4 g TOTM/100 g PVC powder, which translates to a resin pore volume of 0.3 cm³/g, identical to that determined from ESO absorption in the same PVC resin.¹⁹ By adjusting for the amount of plasticizer taken up by the pores, the effective amount of plasticizer absorbed in the matrix polymer was determined, as depicted in Figure 1(b). Over a prolonged period of time at 40°C, there was very little uptake of plasticizer in the polymer matrix. However, at temperatures close to or above the T_g of the PVC resin (83°C—as determined previously by differential scanning calorimetry),¹⁹ significant absorption of TOTM in the polymer was observed.

Figure 2 shows the comparative absorption of TOTM, ESO and mixtures thereof in PVC at elevated temperatures. Similar to the findings with ESO,¹⁹ the following three regions were clearly evident in all the sorption curves at a test temperature of 80°C: (a) “induction” phase corresponding to penetration of the pericellular membrane by the plasticizer and rapid filling of the voids in the polymer, characterized by only slight plasticizer absorption in the matrix polymer; (b) subsequently rapid uptake of plasticizer as the T_g of the polymer presumably fell below 80°C due to plasticizer diffusion, resulting in “swelling” of the particles and agglomerates that constitute the PVC grain; and (c) “saturation” phase in which the swelling was completed and the uptake of plasticizer approached an asymptotic value, representative of the equilibrium solubility of the plasticizer in PVC. TOTM yielded the longest induction time and least

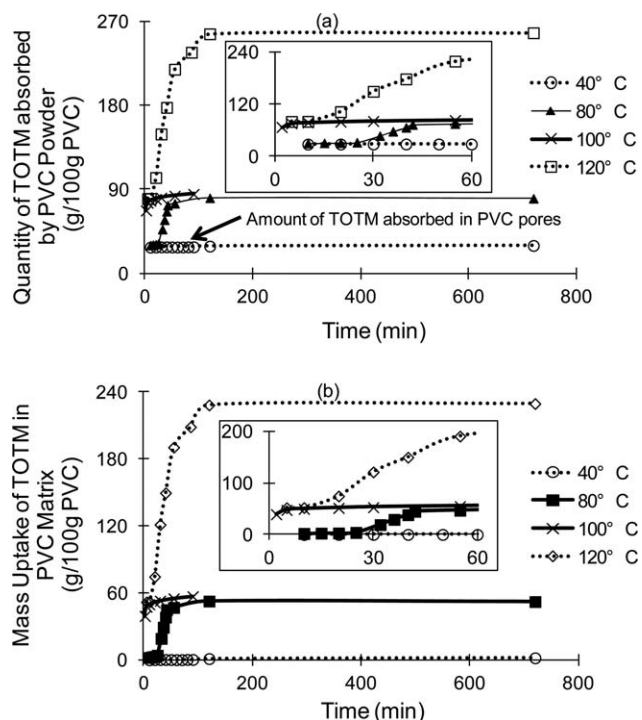


Figure 1. Absorption of TOTM at 40°C to 120°C in: (a) PVC powder; and (b) PVC matrix.

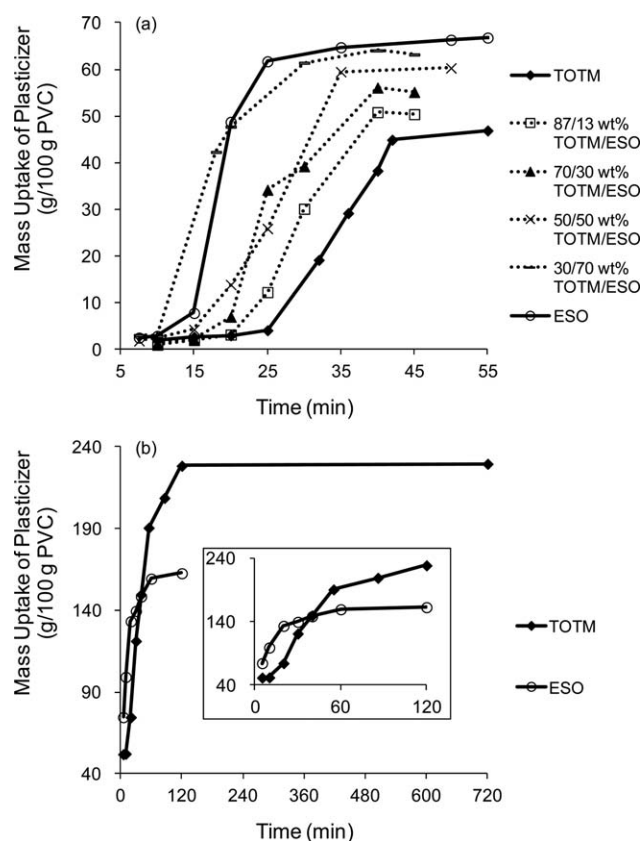


Figure 2. Comparative absorption of TOTM, ESO and mixtures thereof in PVC matrix at: (a) 80°C; and (b) 120°C.

absorption, and ESO the shortest induction time with most absorption, with the performance of the mixtures generally falling in-between. Interestingly, ESO absorbed substantially faster than TOTM in the matrix polymer at 80°C, and mixing even a minor amount of ESO with TOTM enhanced the rate of absorption, even though the bioplasticizer was of relatively higher molecular weight and viscosity.^{22–24} The nonadditive effect of plasticizer composition on uptake was particularly evident after 40 min (Figure 3).

The equilibrium solubility of TOTM at 80°C was 53 g/100 g PVC [Figure 1(b)], less than that of ESO, which was 72 g/100 g PVC.¹⁹ However, at a test temperature of 120°C [Figure 2(b)],

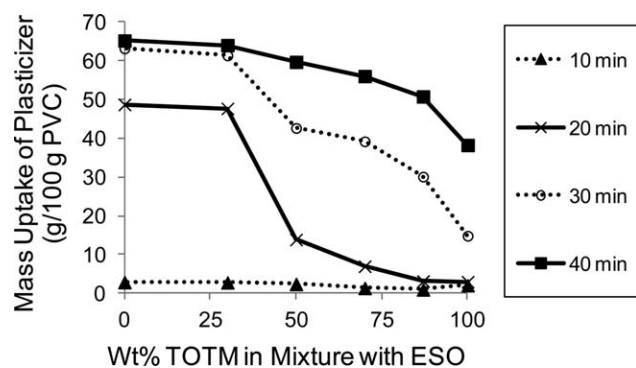


Figure 3. Mass uptake of TOTM, ESO, and mixtures thereof in PVC matrix at 80°C.

there was a reversal in the trend with TOTM exhibiting much higher equilibrium solubility (230 g/100 g PVC) than ESO (163 g/100 g PVC), despite the fact that the rate of absorption was initially faster with the latter, particularly over the first 20 min. A possible explanation for these observations might be partial oxirane ring opening of ESO over a few hours at 120°C, but not at 80°C, catalyzed by the acid arising from dehydrochlorination of PVC.¹⁹ Note that no heat stabilizers were used for the Centrifuge Plasticizer Absorption measurements. Microscopy investigations revealed the changing morphology of PVC grains due to absorption of plasticizer, at a test temperature of 80°C. The porous PVC grains, approximately 150 μm in diameter and composed of aggregates of primary particles of varying sizes, were swollen by either plasticizer entering the pores and absorbing in the polymer matrix, but did not result in the pronounced sintering that was observed with ESO at a higher temperature of 120°C.¹⁹

What these results convey is that, if ESO is imbibed into PVC as a plasticizer at temperatures around 120°C, the amount used should be such that absorption is completed within the first 20 minutes or so, especially if no heat stabilizers are present to minimize dehydrochlorination of the polymer (if indeed the comparatively decreased equilibrium solubility of ESO in PVC at the higher temperature was due to degradation of the bioplasticizer). Furthermore, since relatively superior absorptive characteristics were observed with ESO at a temperature of 80°C, conducting the plasticizer absorption step at this lower temperature would be another means to minimize degradation of the polymer and any associated loss in integrity of the bioplasticizer structure. It is also worth noting that the high solubility of ESO in PVC is consistent with literature measurements showing that the solubility parameters of ESO and PVC at a temperature of 90°C are reasonably close.²⁵ Of course, TOTM is routinely used as a plasticizer for PVC, and there is also a good match of its solubility parameter¹ with that of PVC.²⁵

Plasticizer uptake assessments using a torque rheometer, with heat stabilizer and antioxidant in the PVC composition, revealed that TOTM yielded slower and less of an increase in torque than ESO at set temperatures of 80°C and 120°C. Correspondingly, the rise in temperature was also slower, and less in absolute terms, than that obtained with ESO. These results were consistent with comparatively more rapid and efficient plasticizer uptake of the bioplasticizer. At a set metal temperature of 80°C and mixer speed of 30 rpm (Figure 4), TOTM resulted in largely free-flowing dry powder, with very little (if any) evidence of sintering of the grains, as the final temperature of the composition was only slightly greater than the T_g of the initially unplasticized polymer. However, raising the mixer speed to 60 rpm at this set temperature resulted in a partially fused composition, consistent with increased shear-heating leading to significantly higher temperature. A set temperature of 120°C with this plasticizer resulted in partial sintering at 30 rpm as well as fusion at 60 rpm. Dry blend characteristics could not be deduced for the TOTM compositions, as had earlier been determined for the ESO formulations,¹⁹ since the torque curves were not very well defined. With both materials, increased mixer speed led to faster and greater increases in torque as the

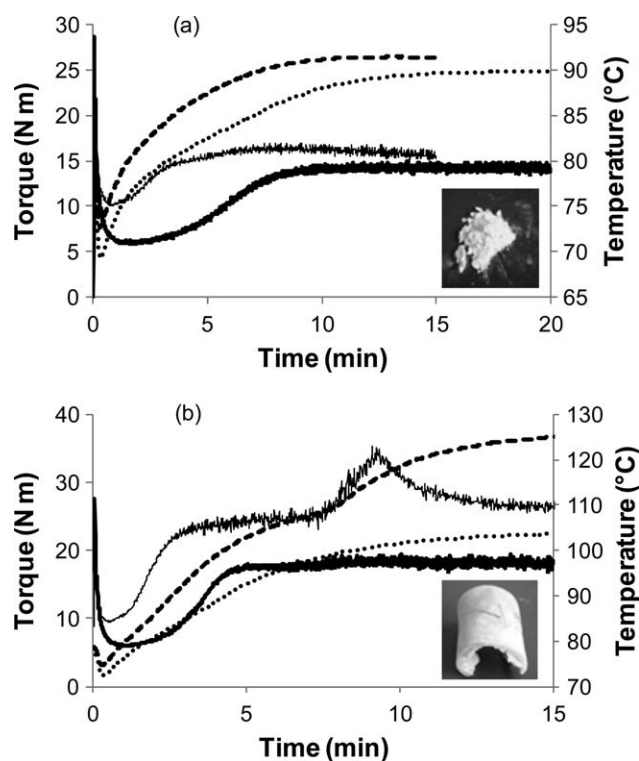


Figure 4. TOTM and ESO Uptake in PVC at 80°C: (a) 30 rpm; (b) 60 rpm—images of TOTM specimens (—TOTM torque; —ESO torque; ····TOTM temperature; - - - ESO temperature).

lubricating effects of the plasticizers decreased due to absorption in the polymer.

Mass losses from molded specimens of plasticized PVC formulations, when in contact with activated carbon, were determined as functions of time, temperature and plasticizer composition (Figure 5). Of course, in addition to TOTM and ESO, other additives or degradation products could have contributed to the mass losses. However, like the torque rheometer studies, these migration assessments were conducted on compositions that contained heat stabilizer and antioxidant. Thus, it is reasonable to expect that degradation of PVC and ESO, as well as consequent network formation, would largely have been mitigated since it is known that ESO can only form network structures during prolonged heat aging of plasticized PVC compositions when heat stabilizers are not used.^{15,19} No appreciable mass loss was observed with any composition up to 96 h at 40°C, which was below the T_g of the plasticized polymer specimens (45°C with TOTM; 54°C with ESO; 53°C with 30 wt % ESO in a mixture with TOTM; and 54°C with 50 wt % ESO in a mixture with TOTM). In contrast, at test temperatures above T_g , measurable migration to activated carbon was observed, with TOTM yielding significantly greater mass loss than ESO (consistent with the differences in molecular weights of the plasticizers). It is also interesting to observe that even a minor amount of ESO in a mixture with TOTM led to synergistic reduction in mass loss.

The temperature-, time-, and composition-dependent changes in hardness of the specimens used for the migration test are given in Figure 6. The standard deviations of the various hard-

ness measurements ranged from ± 0.1 to ± 0.8 . The initial Shore D hardness (i.e., after compression molding, 0 h in the migration test) of the TOTM specimen was 49.5 ± 0.6 , identical to that attained with ESO.¹⁹ Unlike the mass measurements, a noticeable increase in hardness was evident even at the lowest aging temperature of 40°C. The reason for this is not known, but it might be attributed to re-ordering and compaction of the plasticized structure as the polymer chains moved relative to one another over time (since this test temperature was close to the T_g of the plasticized specimens) and a possible increase in lamellar crystal thickness of the polymer, as observed in a previous study on annealing of plasticized PVC.²⁶ The hardness values tended to increase over time at all three temperatures, but with TOTM as plasticizer, there was not as much of a difference between the 80°C and 120°C measurements as would have been expected from the mass loss results. While TOTM resulted in greater increase in hardness over time at elevated temperatures than ESO, the mixtures of the plasticizers yielded nonadditive effects. When aged at 80°C, a minor amount of ESO in the mixture with TOTM was observed to lead to greater hardness increase than TOTM by itself and, upon aging at 120°C, all the mixture combinations yielded much harder specimens than the individual components. These data are not fully understood, and are at odds from the trends seen in the mass loss measurements. Be that as it may, the data do indicate interesting effects of the plasticizer mixtures on annealing characteristics of the plasticized compositions at temperatures above T_g . Figure 7 highlights the conflicting effects of the plasticizer mixtures on mass loss and hardness at an aging temperature of 120°C, i.e.,

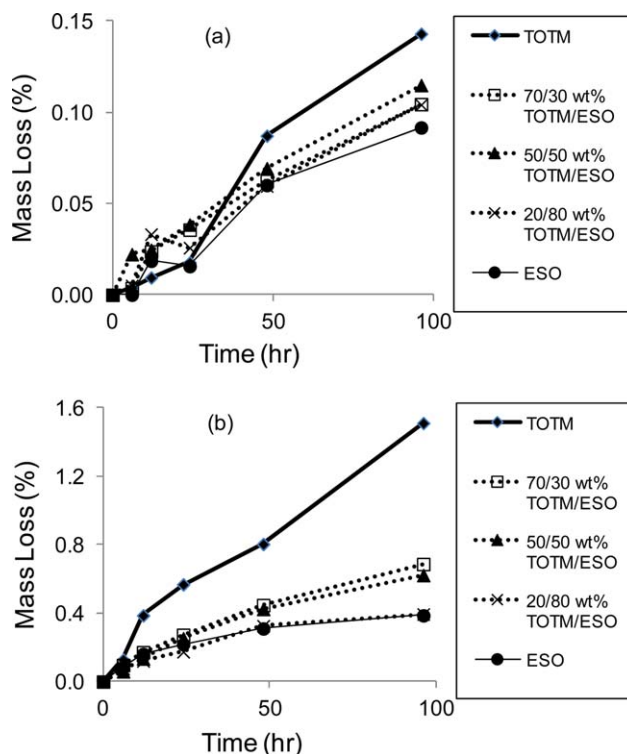


Figure 5. Composition- and time-dependent migration from plasticized PVC at different temperatures: (a) 80°C; and (b) 120°C.

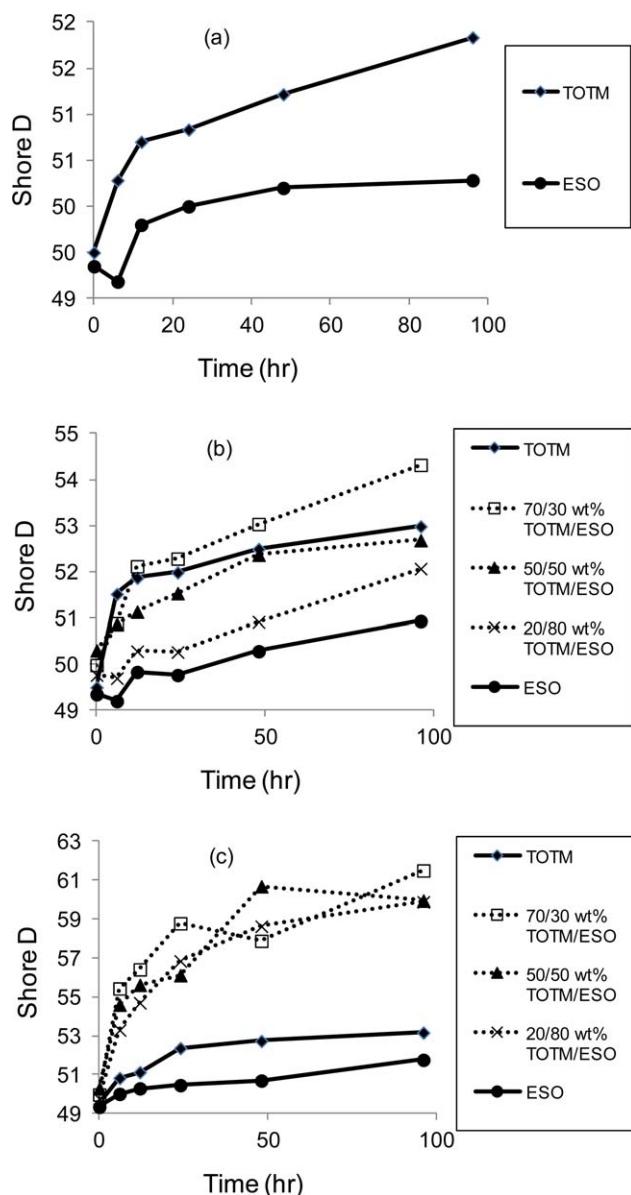


Figure 6. Composition- and time-dependent changes in hardness of plasticized PVC at different temperatures: (a) 40°C; (b) 80°C; and (c) 120°C.

synergistically lower mass losses combined with unexpectedly greater increases in hardness. Furthermore, both ESO and TOTM yielded similar plasticization efficiencies despite large differences in their molecular weights,^{22–24} as evident from the hardness values of unaged specimens (i.e., at 0 h). The 96 h measurements at 120°C indicate that substantially higher mass losses occurred when the proportion of TOTM in the plasticizer composition was greater than 70 wt %. With ESO as the single plasticizer, the very low values of mass loss observed after thermal aging (and correspondingly little change in hardness) suggest that there was not a loss in its effectiveness in the stabilized polymeric composition.

One hypothesis to explain the unusual results depicted in Figure 7 may be interesterification reactions between ESO and TOTM that become more significant at higher temperatures. The prod-

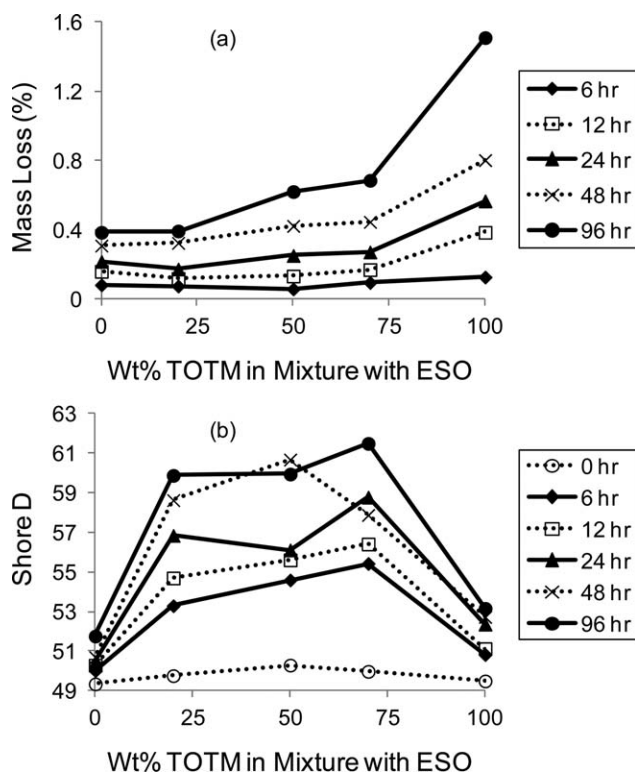


Figure 7. Composition- and time-dependent changes of plasticized PVC at 120°C: (a) mass loss; and (b) hardness.

ucts of such reactions would be of relatively higher molecular weights, which would be consistent with the lower mass losses at prolonged time observed with TOTM/ESO mixtures in comparison with TOTM alone [Figure 7(a)] and corresponding reductions in plasticization efficiencies or increases in hardness [Figure 7(b)]. Given the deleterious effects of the TOTM/ESO mixtures on hardness after heat aging, it would be preferable to substitute ESO for all of the conventional trimellitate plasticizer (instead of employing their mixtures) in applications such as wire and cable insulation where high service temperatures are encountered.

The colors of molded specimens of the plasticized PVC compositions that were used for the migration test are shown in the Supporting Information (Figures S1 and S2). It is worth noting that none of the formulations resulted in significant discoloration after melt blending for 5 min at 165°C and compression molding for 10 min at 180°C. Although the molded specimens aged at 40°C did not change color over the duration of the test, those exposed to higher temperatures did in fact undergo color changes. However, the compositions containing varying amounts of ESO were no more prone to discoloration than the TOTM formulation when aged at 120°C. Additionally, even after 96 h at this temperature, none of the specimens had turned black in color (which would have been evidence of severe levels of decomposition). These results, combined with the fact that the hardness values of the specimens did not increase dramatically under the test conditions, confirm that polymer and plasticizer degradations were largely mitigated by the antioxidant and mixed metal soap present in the

compositions. Note that the metal soap used herein was of a type that is particularly effective at stabilizing ESO plasticized PVC compositions.²⁷ Furthermore, other newer thermal stabilizers have also been shown to be useful in such systems.^{28,29}

CONCLUSIONS

The rate of absorption of TOTM in PVC was less than that of ESO at a temperature of 80°C, but not at a temperature of 120°C. The trimellitate was also relatively less soluble in the polymer than ESO at 80°C (with their mixtures showing intermediate performance), but the converse was true at 120°C. The equilibrium solubilities of TOTM were 53 and 230 g/100 g PVC at 80°C and 120°C, respectively. Those of ESO were 72 and 163 g/100 g PVC at 80°C and 120°C, respectively.

Both ESO and TOTM exhibited similar plasticization efficiencies with stabilized polymeric compositions, even though their molecular weights were very different. As expected, migration out of plasticized and stabilized PVC generally increased with increasing temperature and time, with TOTM yielding significantly greater mass loss than the bioplasticizer (due to the relatively lower molecular weight of the former). Additionally, mixing even a minor amount of ESO with TOTM resulted in synergistically decreased mass loss at elevated temperatures, such that migration out of the plasticized polymer was significantly curtailed with 30 wt % or more of ESO in the plasticizer composition. Surprisingly, although TOTM resulted in more of an increase in hardness over time at elevated temperatures than ESO, the TOTM/ESO mixtures yielded even greater increases in hardness after aging of the plasticized materials at 120°C. Especially noteworthy is the fact that, with ESO as the sole plasticizer, there was not significant deterioration in its efficacy during thermal aging of the stabilized composition. Furthermore, the compositions comprising ESO were no more prone to discoloration than the TOTM formulation during thermal aging. Thus, ESO can effectively be used to substitute part or all of conventional trimellitates in plasticized PVC compositions. However, for wire and cable applications (which require retention of mechanical properties after heat aging for prolonged periods of time), it would be preferable to use ESO as the single plasticizer.

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