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PLASTICIZING EFFECT OF SUCROPALMITATE ON POLYVINYL CHLORIDE: STUDY BY DIFFERENTIAL SCANNING CALORIMETRY AND SCANNING ELECTRON MICROSCOPY

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Abstract
Sucropalmitate lowers the glass transition temperature (T_g) of polyvinyl chloride by 6.9 °C at 10 wt.% and by 10.9 °C at 20 wt.%, but above 20 wt.% it separates into a distinct phase. Films of unstabilized PVC containing 0, 10, 20, 40 and 60 % sucropalmitate (SP70), prepared by solution casting from tetrahydrofuran, were investigated. Their thermal behavior was studied by differential scanning calorimetry (DSC) in argon at 10 K/min in two heating cycles.
In the second heating, T_g (midpoint) decreases from 79.7 °C for pure PVC to 72.8 °C (10 %) and 68.8 °C (20 %). At 20 %, a weak endothermic effect appears around 50 °C, and at 40 and 60 % a pronounced endothermic peak with a maximum around 53 °C appears, overlapping the glass transition step. Scanning electron microscopy (SEM) confirms these results: the surface of the films with 10 and 20 % is smooth and homogeneous, at 40 % a cellular network of ridges with 30–60 µm cells is formed, and at 60 % the surface is highly heterogeneous, with aggregates and filamentous formations of the separated ester phase. The results show that sucrose palmitate is an effective and compatible plasticizer up to about 20 wt.%, and at higher concentrations its compatibility with PVC is limited.

Keywords: polyvinyl chloride, sucrose esters, sucrose palmitate, plasticizer, differential scanning calorimetry, scanning electron microscopy, glass transition temperature, compatibility.

1. INTRODUCTION

Polyvinyl chloride (PVC) is one of the most widely used thermoplastics, but in its neat state it is hard and brittle, with a glass transition temperature of around 80 °C. To obtain flexible products, plasticizers are added, which increase the free volume and chain mobility and lower T_g [1, 2, 8].

For a long time, the main PVC plasticizers have been phthalate esters, most notably di(2-ethylhexyl) phthalate (DEHP). Their migration from finished articles and proven adverse health effects have led to regulatory restrictions and to a search for alternatives from renewable sources [2, 3]. A promising group are sucrose esters, nonionic surfactants derived from sucrose and fatty acids, which are biodegradable, non-toxic and approved for use in food, cosmetics and pharmaceuticals [4].

The sucrose ester molecule combines a hydrophilic sucrose moiety and a hydrophobic fatty acid chain. The ester groups can interact with the polar C–Cl bonds of PVC, while the alkyl chain can keep the macromolecules apart; both are prerequisites for plasticizing action. However, the efficiency and compatibility limit of such a plasticizer must be determined experimentally.

Differential scanning calorimetry (DSC) is a standard method for assessing the plasticizing effect. The decrease in T_g reflects the degree of plasticization, while a

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single glass transition step and the absence of phase transitions of the plasticizer itself are criteria for compatibility of the two components [1, 5].

Scanning electron microscopy (SEM) complements the calorimetric data by directly revealing the surface morphology and any separated plasticizer phase.

The aim of the present work is to evaluate by DSC and SEM the plasticizing effect of sucrose palmitate on PVC in the range of 10–60 wt.% and to determine the limit of its compatibility with the polymer.

2. MATERIALS AND METHODS

2.1. Materials

Commercial polyvinyl chloride without colorants, stabilizers and fillers was used. Sucrose palmitate SP70 was tested as a plasticizer. Tetrahydrofuran (THF) was used as a solvent.

2.2. Film preparation

PVC films with sucrose palmitate contents of 10, 20, 40 and 60 % were prepared by casting from tetrahydrofuran solution. A PVC film without plasticizer was prepared as a control.

The required amount of PVC was weighed on an analytical balance into a 150 cm³ beaker, and 100 cm³ of tetrahydrofuran was added. The mixture was heated in a water bath at 40 °C until the polymer had completely dissolved, after which the weighed amount of sucrose palmitate was added. The solution was stirred with a magnetic stirrer for 2 h until fully homogenized, poured into a Petri dish and left until the solvent had evaporated. The film was dried at room temperature in a vacuum dryer.

2.3. Differential scanning calorimetry

Measurements were performed on a NETZSCH DSC 204 F1 Phoenix with a type E sensor. Samples weighing 2.5–5.9 mg were placed in aluminum crucibles with pierced lids, with an empty crucible as reference. Argon was used as purge and protective gas, each at a flow rate of 20 ml/min. The instrument was calibrated for temperature and sensitivity in argon at 10 K/min, and the measurements were baseline-corrected.

The temperature program comprised two heating cycles at 10 K/min:

1. First heating from 20 to 200 °C, reflecting the state of the film after preparation (thermal history, residual solvent);
2. Cooling to −50 °C;
3. Second heating from −50 to 200 °C, used to determine the glass transition temperature after the thermal history had been erased.

T_g was determined with the NETZSCH Proteus software by the step method, reporting the onset, midpoint (half step height), inflection and end temperatures and the change in specific heat capacity ΔC_p [5]. The T_g midpoint was used to compare the samples. Thermograms are plotted with endothermic effects upward.

2.4. Scanning electron microscopy

The surface morphology of the films with 10, 20, 40 and 60% sucrose palmitate was examined with a scanning electron microscope at an accelerating voltage of 10 kV and magnifications of ×200 to ×3700. Two imaging modes were used:

- **secondary electron imaging (SEI)** — contrast is mainly determined by surface relief;
- **backscattered electron imaging (BEC)** — the contrast also depends on the average atomic number of the material [9]. Because PVC contains chlorine (Z = 17), PVC-rich regions appear brighter than regions rich in sucrose ester, which contains only C, H and O.

3. RESULTS AND DISCUSSION

The DSC thermograms of the five samples are shown in Fig. 1, and the glass transition parameters from the second heating are given in Table 1.

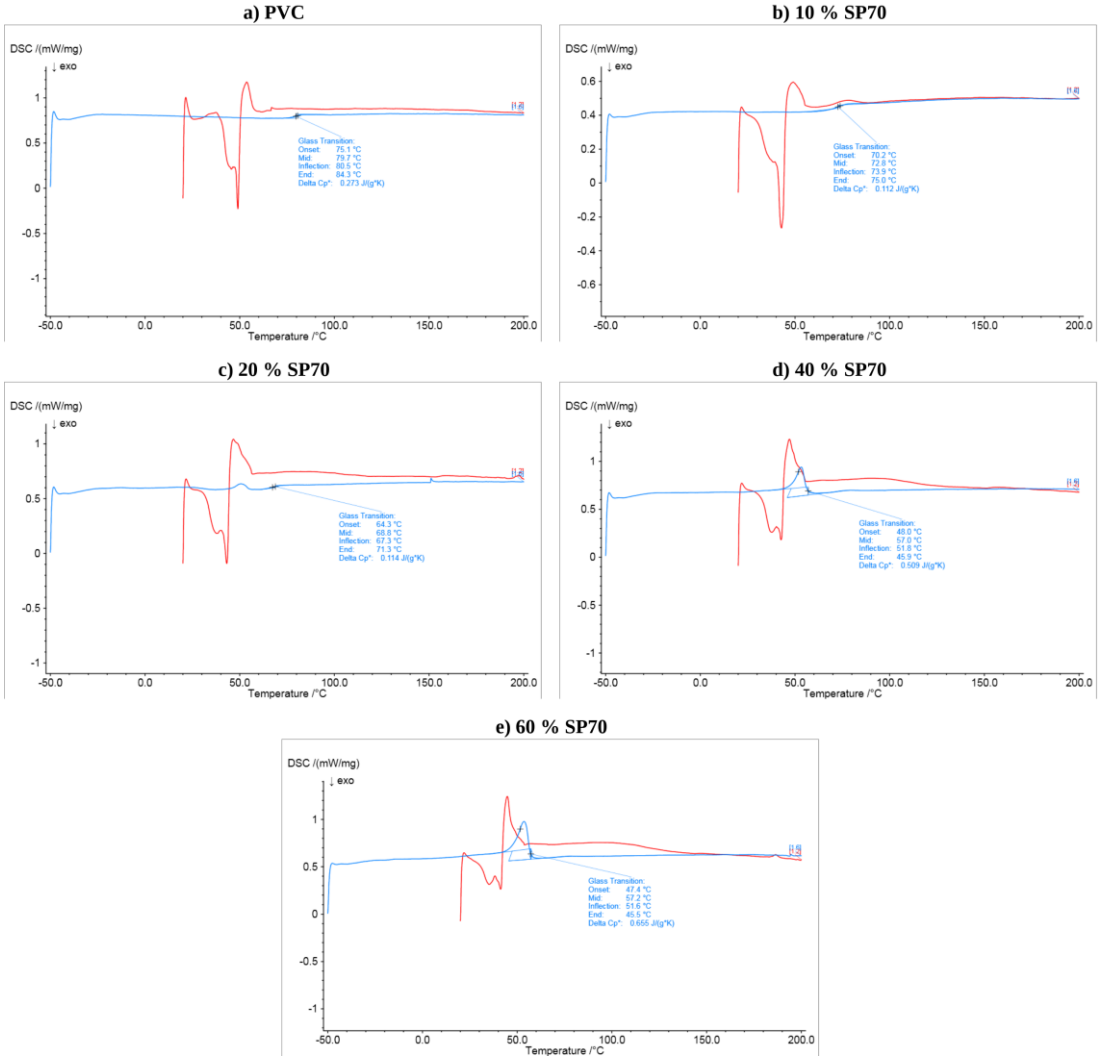


Fig. 1. *DSC thermograms of PVC films: a) without plasticizer; b) 10%; c) 20%; d) 40%; e) 60% sucrose palmitate. Red: first heating (20–200 °C); blue: second heating (−50 to 200 °C); 10 K/min, Ar, endothermic effects upward.*

Table 1. *Glass transition parameters of PVC films from the second heating (10 K/min, Ar)*

Sample	SP70, %	Mass, mg	T_g onset, °C	T_g mid, °C	T_g inflection, °C	T_g end, °C	ΔC_p, J/(g K)	ΔTg mid, °C
PVC X	0	2.5	75.1	79.7	80.5	84.3	0.273	—
DVF_6_10%_SP70	10	5.9	70.2	72.8	73.9	75.0	0.112	−6.9
DVF_6_20%_SP70	20	3.7	64.3	68.8	67.3	71.3	0.114	−10.9
DVF_6_40%_SP70	40	3.8	48.0*	57.0*	51.8*	45.9*	0.509*	(−22.7)*
DVF_6_60%_SP70	60	4.2	47.4*	57.2*	51.6*	45.5*	0.655*	(−22.5)*

* Values from the automatic evaluation that do not describe the glass transition of PVC: the step overlaps with an endothermic peak (Section 3.4), the end temperature is lower than the onset temperature, and ΔC_p exceeds that of the neat polymer. ΔTg mid is relative to neat PVC.

3.1. First heating

On first heating, all films, including neat PVC, show a complex effect between 30 and 60 °C: an exothermic deflection followed by an endothermic peak. The minimum shifts from about 49 °C for neat PVC to 41–43 °C for the films with sucrose palmitate, and the peak maximum from about 54 °C to 44–49 °C.

Since the effect is also observed in the film without plasticizer, it is mainly associated with the non-equilibrium state of the material after casting: release of residual

tetrahydrofuran (b.p. 66 °C), relaxation of internal stresses and enthalpic relaxation of the glassy phase [6]. In plasticized films, melting of sucrose ester crystallites probably also contributes. The shift of the effect to lower temperatures with the addition of ester also indicates increased chain mobility. Unambiguous separation of these contributions requires thermogravimetric analysis to quantify the residual solvent.

For neat PVC, the first heating curve gradually deviates downward above 150 °C. Since the polymer contains no stabilizers, this may indicate the onset of thermal degradation (dehydrochlorination), which should be considered when choosing the upper temperature of the program.

3.2. Glass transition temperature at 10 and 20% sucrose palmitate

After the thermal history has been erased, all samples show a single glass transition step, and T_g decreases consistently with increasing ester content. The T_g midpoint drops from 79.7 °C for neat PVC to 72.8 °C at 10 % and 68.8 °C at 20 %. The value for the neat polymer agrees with literature data for PVC [1].

The plasticizing efficiency, expressed as the decrease in T_g per 1 % of ester, is 0.69 °C/% at 10 % and 0.55 °C/% at 20 %. Its decrease with concentration indicates saturation of the ester–polymer interaction.

To evaluate the behavior of the blends, the Fox equation [7] was applied:

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \qquad (1)$$

where w_1 and w_2 are the mass fractions of PVC and plasticizer, and T_g is in K. The effective T_g of sucrose palmitate back-calculated from the measured values is about 294 K (21 °C) at 10 % and about 304 K (31 °C) at 20 %. The increase of the calculated value with concentration confirms the deviation from ideal additivity and the decreasing efficiency. The calculation assumes that the percentages are relative to the total mass of the film.

3.3. Change in heat capacity

ΔC_p at the glass transition decreases from 0.273 J/(g K) for neat PVC to 0.112–0.114 J/(g K) for films with 10 and 20 % ester. Normalized per gram of PVC, it is 0.124 and 0.143 J/(g K), i.e. about half the value for the neat polymer.

A smaller ΔC_p suggests that part of the transition lies outside the evaluation interval. Plasticized PVC usually has a broader and asymmetric glass transition region, part of which may fall outside the selected evaluation limits; for low-mass samples, baseline accuracy also plays a role. ΔC_p should therefore be interpreted only qualitatively.

In the second-heating curve of the 20 % film, a weak endothermic effect appears around 50 °C, which is absent at 10 %. It is the first sign of separation of an ester-rich phase.

3.4. Phase separation at 40 and 60% sucrose palmitate

At 40 and 60 %, the second heating shows a pronounced endothermic peak with a maximum around 53 °C, larger at 60 %. Since the peak reappears after cooling, it corresponds to a reversible transition (melting) of a separate, probably partially crystalline, sucrose palmitate phase. Its position is in the range characteristic of the melting of sucrose esters with saturated fatty acid residues [4].

The peak overlaps with the glass transition step, and the automatic evaluation gives physically inconsistent results: an end temperature below the onset and a ΔC_p of 0.51–0.66 J/(g K), above the value for neat PVC. Therefore, the values in Table 1 for these samples are not the true T_g of the polymer phase. The two samples have practically the same apparent T_g (57.0 and 57.2 °C), which also indicates that above a certain concentration the excess ester does not dissolve in the polymer.

To separate the glass transition from melting, modulated DSC, DSC of neat sucrose palmitate under the same conditions and dynamic mechanical analysis of the films are recommended.

3.5. Surface morphology (SEM)

The SEM images confirm the DSC results: up to 20 % the surface is

homogeneous, whereas at 40 and 60 % a distinct structure appears. Secondary electron images are shown in Fig. 2, backscattered electron images in Fig. 3, and the main observations are summarized in Table 2.

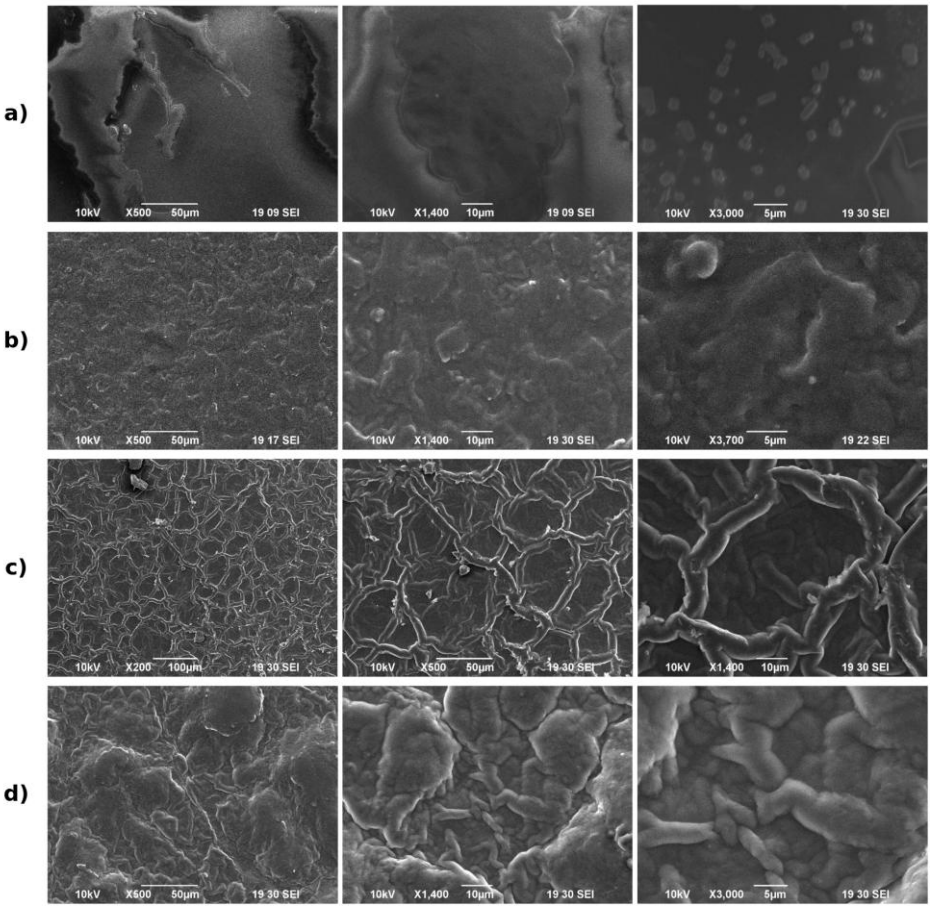


Fig. 2. *SEM images of the surface of PVC films, secondary electrons (SEI, 10 kV): a) 10 % (×500, ×1400, ×3000); b) 20 % (×500, ×1400, ×3700); c) 40 % (×200, ×500, ×1400); d) 60 % (×500, ×1400, ×3000) sucrose palmitate.*

Table 2. *Surface morphology of PVC films from SEM*

SP70, %	Secondary electrons (SEI)	Backscattered electrons (BEC)	Assessment
10	Smooth, featureless matrix; occasional film folds; isolated particles 0.5–1.5 μm in size	No clear compositional contrast in the matrix; particles visible mainly through topography	Homogeneous system; isolated surface inclusions
20	Uniform fine microrelief; isolated globules 2–5 μm; no distinct phase regions	Nearly uniform signal; faint, diffuse brighter spots	Homogeneous system; onset of heterogeneity
40	Cellular network of ridges; cells 30–60 μm, ridges about 3–5 μm wide; fine secondary folds within cells	Network visible as thin, brighter lines on a uniform background	Distinct supramolecular structure associated with phase separation
60	Rough, uneven surface; aggregates 20–50 μm with filamentous, helically twisted formations 1–2 μm thick between them	Brighter lines and spots at aggregate boundaries	Pronounced phase separation; ester-rich phase dominates the surface

Films with 10% sucrose palmitate. In secondary electrons, the surface is smooth and featureless (Fig. 2a). The distinct folds and edges at low magnification are topographic features of the film itself, formed during drying or on removal from the substrate. At ×3000, isolated particles of regular, often rectangular shape and 0.5–1.5 μm in size are observed locally. Their shape suggests a crystalline origin, probably small

ester crystallites brought to the surface during solvent evaporation. In backscattered electrons (Fig. 3a), the matrix shows no pronounced compositional contrast. The strong bright and dark zones at ×1400 follow the topography and result from tilt and edge effects rather than from compositional differences. The particles are isolated and do not form a continuous phase, consistent with the single glass transition step in DSC.

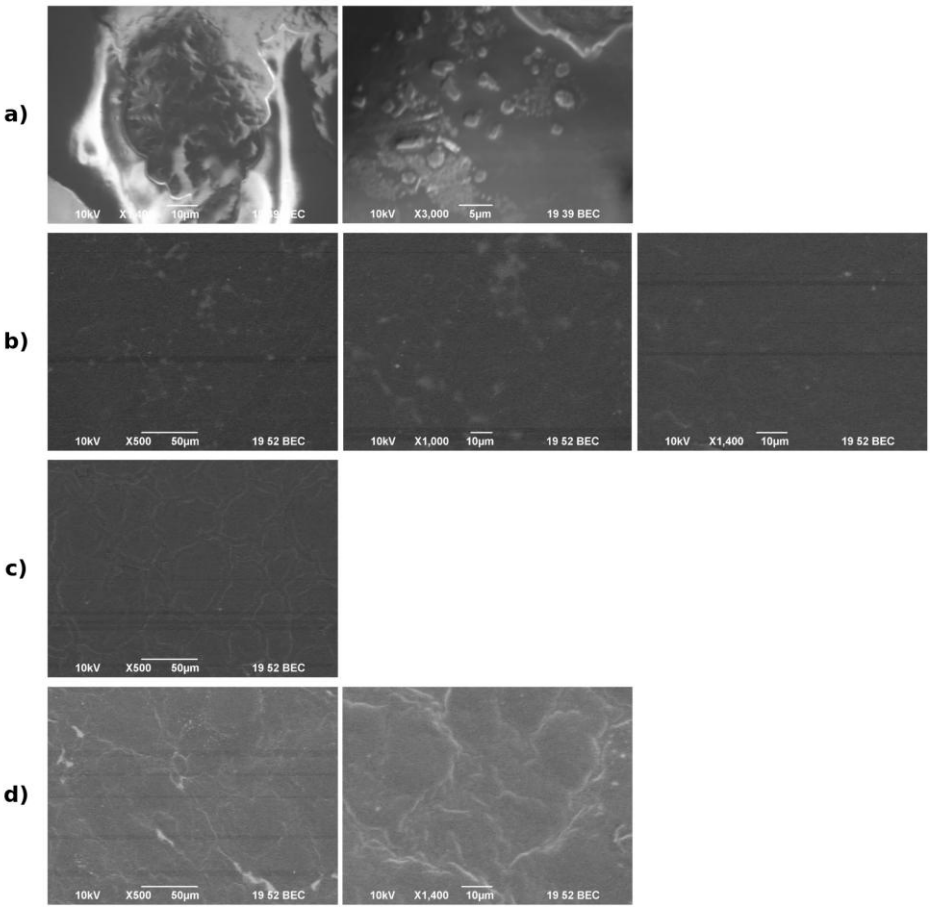


Fig. 3. *SEM images of the surface of PVC films, backscattered electrons (BEC, 10 kV): a) 10 % (×1400, ×3000); b) 20 % (×500, ×1000, ×1400); c) 40 % (×500); d) 60 % (×500, ×1400) sucrose palmitate.*

Films with 20% sucrose palmitate. The surface is uniform, with fine microrelief and isolated globular formations 2–5 μm in size (Fig. 2b). No distinct second-phase regions are observed. In backscattered electrons, the signal is nearly uniform, with a few faint brighter spots (Fig. 3b). The film remains homogeneous on the micrometer scale. The appearance of globules corresponds to the weak endothermic effect around 50 °C in the second heating and indicates that this composition is close to the compatibility limit.

Films with 40% sucrose palmitate. The morphology changes abruptly (Fig. 2c). A cellular network of protruding ridges covers the entire surface. The cells are 30–60 μm in size and the ridges about 3–5 μm wide. Finer secondary folds are present inside the cells, together with isolated particles and aggregates on the surface. Similar cellular structures form during solvent evaporation from polymer solutions when convection cells are fixed by phase separation. The separated ester phase is probably concentrated at the cell boundaries. In backscattered electrons, the network is visible only as thin bright lines against a uniform background (Fig. 3c). These lines may arise from the ridge topography as well as from compositional differences; distinguishing between them requires EDS chlorine mapping.

Films with 60% sucrose palmitate. The surface is highly heterogeneous (Fig. 2d). Large aggregates 20–50 μm in size with a rough internal texture are observed. Between them are filamentous, helically twisted formations 1–2 μm thick and 5–15 μm long. Such formations are characteristic of the self-assembly of amphiphilic molecules into crystalline or liquid-crystalline structures and are direct morphological evidence of a separated sucrose palmitate phase. In backscattered electrons, brighter lines and spots are visible at the boundaries of the aggregates (Fig. 3d).

Comparison with DSC. The morphological changes agree with the calorimetric results. At 10 and 20 %, where DSC shows a single glass transition step, the surface is homogeneous. At 40 and 60 %, where the endothermic peak around 53 °C appears, SEM shows distinct structures of the separated ester phase. Both methods place the compatibility limit between 20 and 40 %.

SEM characterizes only the surface. Since surfactant molecules may accumulate at the surface during solvent evaporation, the bulk morphology may be more homogeneous. Examination of cryofractured cross-sections and EDS chlorine mapping are therefore recommended.

4. CONCLUSIONS

1. Sucrose palmitate (SP70) plasticizes polyvinyl chloride: at 10 and 20%, the T_g midpoint decreases by 6.9 and 10.9 °C, respectively, relative to neat PVC (79.7 °C), with a single glass transition step.
2. The plasticizing efficiency decreases from 0.69 to 0.55 °C per 1 % of ester, and the system deviates from ideal additivity according to the Fox equation.
3. A weak endothermic effect around 50 °C at 20 % and a pronounced peak around 53 °C at 40 and 60 % indicate separation of a distinct sucrose ester phase. The compatibility limit of sucrose palmitate with PVC is between 20 and 40 %, with the first signs of phase separation appearing around 20 %.
4. At 40 and 60 %, automatic T_g evaluation is unreliable because the glass transition overlaps with the endothermic peak; modulated DSC or DMA is required for these compositions.
5. SEM confirms the compatibility limit: the surface is homogeneous at 10 and 20%, at 40 % a cellular network of ridges forms (cells 30–60 μm), and at 60 % aggregates and filamentous formations of the separated ester phase appear.
6. Sucrose palmitate is a promising biodegradable and non-toxic plasticizer for PVC at contents up to about 20 %, including as a component of plasticizer blends.

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