

## Effects of diffusion of a naturally-derived plasticizer from soft PVC

Emanuela Calò<sup>a,b</sup>, Antonio Greco<sup>a,\*</sup>, Alfonso Maffezzoli<sup>a</sup>

<sup>a</sup> Department of Engineering for Innovation, University of Salento, Via per Monteroni, 73100 Lecce, Italy

<sup>b</sup> ENEA - Italian National Agency for New Technologies, Energy and the Environment-Advanced Physical Technologies and New Materials Dept., S.S. 7 - Km 714, 72100 Brindisi, Italy

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### ABSTRACT

Soft PVC was obtained by using a new plasticizer, based on cardanol, a renewable resource characterized by chemical and physical properties very close to those of diethylhexyl phthalate (DEHP). Cardanol acetate (CA) was obtained by solvent free esterification of cardanol, and used as secondary plasticizer, by partial substitution of DEHP in soft PVC formulations. Ageing tests were performed in order to study the stability of properties of the soft PVC formulations related to plasticizer diffusion. Tensile properties and hardness changes were used to monitor the macroscopic effects of plasticizer diffusion. Soft PVC obtained by partial substitution of DEHP by CA showed a significant modification of mechanical properties related to a higher plasticizer evaporation during ageing tests. Migration tests confirmed that CA is characterized by a higher diffusivity in soft PVC compared to DEHP.

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### 1. Introduction

In 1951, the International Union of Pure and Applied Chemistry (IUPAC) developed a universally accepted definition of a plasticizer as a substance or a material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability, or extensibility [1]. Plasticizers, not chemically bound to PVC, leach out from medical products into those human tissues and blood which come in contact with it [2]. In general, plasticizer can either be extracted during contact with chemically incompatible media, such as water [3–6], or can evaporate [2,7–9]. In recent years new concerns about the toxicological impact of the most used plasticizer for PVC, i.e. diethylhexyl phthalate (DEHP) were raised. Although DEHP is suggested to be of low acute toxicity, various studies indicated that the potential risks associated with DEHP and dioctyl phthalate (DOP) are higher for infants and pregnant women [10,11]. For this reason, most European countries banned the use of phthalates for the fabrication of toys used by children less than 3 years old [12].

As a consequence, different attempts were devoted to the development of innovative plasticizers. Among these, polymeric plasticizers are attracting a growing interest, due to the reduced

toxicity and low leachability [13–19]. Nevertheless, the substitution of DEHP by polymeric plasticizer has some drawbacks, due to the increased viscosity of the plastisol [20], and the higher costs of polymeric plasticizer compared to DEHP [21].

On the other hand, cardanol and its derivatives can be considered nowadays very attractive precursors in order to develop new materials from renewable bio-sources to be used in eco-friendly processes [22–25]. Cardanol presents chemical and physical properties very close to those of DEHP. It is reported that properties of natural rubber (NR) modified with phosphorylated cardanol have been found to be superior to those obtained by DEHP [26]. Also, phosphorylated cardanol has been used as an effective plasticizer for ethylene–propylene–diene rubber [27], polychloroprene and polybutadiene rubber [28], and LLDPE/EVA copolymer blends [29]. Derivatives of cardanol have also been proved to be efficient plasticizers for PVC [30,31]. In particular, in recent work, it has been shown that cardanol acetate, obtained by solvent free esterification of cardanol [32,33], can be used in reduced amounts (lower than 80 phr) as plasticizer for PVC. On the other hand, further epoxidation leads to the formation of a very efficient plasticizer, which shows an unlimited solubility in PVC. Unfortunately, epoxidation of cardanol acetate requires the use of toxic solvents and reagents, which are not considered suitable for the production of a green plasticizer [34]. However, a partial substitution of DEHP with CA can be considered a very interesting alternative for the reduction of the environmental and toxicological impact of soft PVC.

\* Corresponding author.

E-mail address: [antonio.greco@unisalento.it](mailto:antonio.greco@unisalento.it) (A. Greco).

In this work, cardanol acetate, obtained by a solvent free esterification method was used, in partial substitution of DEHP, as secondary plasticizer for PVC, to produce medium scale samples for physical and mechanical characterization. The soft PVC obtained using a mixture of DEHP and cardanol acetate showed thermal and mechanical properties comparable to those of PVC obtained with neat DEHP. Nevertheless, an increased plasticizer volatilization at high temperatures was observed, which caused a lower stability of mechanical properties of soft PVC.

## 2. Materials and methods

A commercial PVC in powder form, Vestolit B7021 (Huls, Germany) and bis-(2-ethylhexyl) phthalate (DEHP) as plasticizer (also from Huls) were adopted. Cardanol was purchased by Oltremare (Bologna, Italy). The catalyst, zinc perchlorate hexahydrate, was purchased from Sigma–Aldrich.

Esterification was performed in a medium scale batch process in order to produce plasticizers in adequate amount for mechanical and physical characterization. This reaction was performed by mixing 1 mol equivalent of cardanol with 1.5 mol equivalent of acetic anhydride, together with 0.015 mol equivalent of zinc perchlorate hexahydrate as catalyst.

All the products were obtained in quantitative yields. The structures of cardanol and cardanol acetate are reported in Fig. 1.

Plasticizer mixtures were obtained by adding different amounts of cardanol acetate to DEHP. Then, soft PVC samples were obtained by mixing the plasticizer with PVC at 180 °C for 15 min in a Haake Rheocord Mixer. The composition of the studied samples is reported in Table 1. All samples are characterized by the same total amount of plasticizer, being only different for the relative content of CA and DEHP.

Soft PVC samples were aged at 105 °C for 5 weeks, while measuring the evolution of weight as well as of thermal and mechanical properties as a function of ageing time.

Differential Scanning Calorimetry (DSC) tests were performed on a Mettler Toledo DSC 622 heating soft PVC samples between –130 and 190 °C at 10 °C/min, then cooling back to –130 °C at 10 °C/min, followed by a second heating step at 10–150 °C. Only the second heating step was considered representative in order to calculate the glass transition temperature of materials.

Tensile properties of soft PVC were obtained in a Lloyd LR5K dynamometer, on dumbbell shaped samples, with a crosshead speed of 20 mm/min.

Shore A hardness tests were performed on a Gibitre Instruments Digital Manual Hardness Check.

Plasticizer evaporation/migration tests were performed on injection moulded soft PVC disks about 1.3 mm thick and 25 mm in

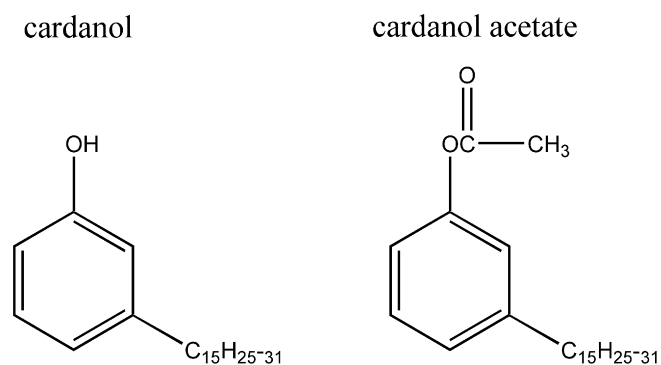


Fig. 1. Chemical structure of cardanol and cardanol acetate.

**Table 1**  
Composition of the soft PVC samples.

	Total plasticizer content (70 phr)	DEHP content	CA content
CA0	41.2%	41.2%	0
CA4	41.2%	37.08%	4.12%
CA8	41.2%	32.96%	8.24%

diameter, by holding at 105 °C, and measuring the evolution of sample weight with a Sartorius analytical balance characterized by an error of  $\pm 0.01$  mg.

## 3. Results and discussion

The glass transition temperatures ( $T_g$ ) of unaged soft PVC samples are reported in Table 2. As it can be observed, the  $T_g$  decreases with increasing CA content, due to the lower  $T_g$  of CA (about –105 °C) compared to DEHP (about –83.5 °C) [34]. As a consequence, at low plasticizer content, the plasticizing efficiency of CA is higher than that of DEHP, in accordance with the Fox, Gordon-Taylor or Couchman–Karasz equations [35,36]. The  $T_g$  of sample CA0 is limitedly affected by the thermal treatment, and a decrease of the glass transition temperature is observed at the beginning of the ageing process. This observation is in agreement with previously reported results, showing a decrease of the hardness of soft PVC at the beginning of the thermal ageing, and can be attributed to a continuous plasticization of the polymer during thermal ageing [34]. After the initial  $T_g$  decrease, the value of the  $T_g$  for sample CA0 increases with ageing time, which is in turn due to some plasticizer loss due to evaporation. Even in this case, the observation is in agreement with the results previously reported, showing that the sample hardness, after reaching a minimum value during thermal ageing, continuously increases, due to plasticizer loss [34]. In contrast to sample CA0, samples CA4 and CA8 show a remarkable increase of  $T_g$  during ageing at 105 °C. This  $T_g$  increase is compatible with a plasticizer desorption, as also confirmed from the results reported in Fig. 2, where the thermograms of sample CA8 and CA0 after thermal ageing are compared. For sample CA0 a single glass transition is observed in Fig. 2, whereas two distinct glass transitions are observed for sample CA8, indicating the formation of two different phases after thermal ageing. During treatment at 105 °C, the plasticizer migration can cause an enrichment in CA on the surface zones of a soft PVC part, whereas the core of the soft PVC part gets enriched in PVC. Therefore, the lower  $T_g$  signal observed in Fig. 2 is relative to a CA rich phase, whereas the higher  $T_g$  signal, reported in Table 2, is relative to a PVC rich phase. The results reported in Table 2 refer to the higher  $T_g$ , that of the PVC rich phase (plasticized PVC).

Mechanical characterization was also performed on soft PVC samples before and after thermal ageing. The results reported in Figs. 3–5 show that the mechanical properties of unaged samples CA4 and CA8 are comparable to those of sample CA0. Nevertheless, substitution of DEHP with CA causes a general increase of the stiffness and strength of soft PVC, and a decrease of the elongation at break. The difference between mechanical properties of soft PVC samples measured after 1 week at 105 °C is lower than the error

**Table 2**  
Glass transition temperatures of soft PVC samples.

	$T_g$ (°C) unaged	$T_g$ (°C) after 1 week at 105 °C	$T_g$ (°C) after 5 weeks at 105 °C
CA0	–32	–36	–33
CA4	–38	–37	–33
CA8	–41	–42	–34

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