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Plasticizer for poly(vinyl chloride) from cardanol as a renewable resource material

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ABSTRACT

The present work is aimed to the preliminary analysis of the applicability of cardanol derivatives as renewable plasticizers for soft PVC. Two different plasticizers were studied, obtained by esterification of the cardanol hydroxyl group (cardanol acetate) and further epoxidation of the side chain double bonds (epoxidated cardanol acetate). Differential Scanning Calorimetry (DSC) was used to study the miscibility between PVC and cardanol derived plasticizers. The miscibility was correlated to the chemical structure of plasticizer by means of the Hansen solubility parameter analysis. Results obtained indicated that esterification of cardanol yields a partial miscibility with PVC, whereas esterification and subsequent epoxidation yield a complete miscibility with PVC. Therefore cardanol acetate, obtained by solvent-free esterification of cardanol, was used as a secondary plasticizer of PVC. Mechanical and rheological analysis showed that the cardanol acetate can partially replace DEHP in PVC formulation.

1. Introduction

In recent years Poly Vinyl Chloride (PVC) has been the subject of severe critics related to its environmental impact. Besides carcinogeneity of vinyl chloride monomer, soft (or plasticized) PVC contains up to 40% by weight of potentially toxic phthalates, which can migrate out of PVC components during service life [1]. Various studies indicated that the potential risks associated with the exposure to the most used plasticizers, di-ethyl-hexyl-phthalate (DEHP) and Di-Octyl-Phtalate (DOP), is presumably higher for infants and pregnant women [2,3]. For this reason, most European countries banned the use of phthalates for the fabrication of toys used by children less than 3 years old [4].

Attempts have been made to reduce the leaching of DEHP, for example by creating hybrid coating on soft PVC tubes [5]. Obviously, this approach has some limitations in the costs involved, and in the product geometries which can be manufactured. A second proposed alternative is given by the crosslinking of PVC, which can decreas the mobility of diffusing species inside the polymer matrix [6–8]. Unfortunately, crosslinking usually involves an unacceptable viscosity increase of the polymer [6,9], and possible degradation of the polymer matrix [6,10]. A third alternative to reduce plasticizer leaching is the use of polymeric type materials as plasticizers. Besides to reduced toxicity, the polymeric plasticizers offer low leachability, due to their high molecular weight [11–16]. Polymeric plasticizers, in turn, usually increase significantly the viscosity of the plastisol [17]. More importantly, polymeric plasticizers are too expensive for most applications involving soft PVC [18].

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[19,20]. Cardanol is obtained by distillation of the Cashew Nut Shell Liquid (CNSL) that is a by-product of cashew industry, a sustainable, low cost and largely available natural resource. 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 [21]. Also, phosphorilated cardanol has been used as an effective plasticizer for ethylene–propylene diene rubber [22], polychloroprene and polybutadiene rubber [23], and LLDPE/EVA copolymer blends [24]. Derivatives of cardanol have also been proved to be efficient plasticizers for PVC [25,26]. Esterification of the hydroxy group of the cardanol molecule is necessary in order to obtain a good miscibility of the cardanol with the base PVC. Miscibility between cardanol and PVC can be further increased by insertion of an epoxy bond on the side chain of cardanol [26]. On the other hand, the evaluation of the cardanol derived plasticizer effectiveness was mainly made on the basis of mechanical characterization. There is no correlation between the plasticizing efficiency and the chemical structure of the plasticizers. Also, the work reported in ref [26] does not address neither the effect of the plasticizer content on the glass transition

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temperature of the mixture, neither the maximum plasticizer content which can be attained before phase segregation occurs.

In this work, the plasticizing effectiveness of cardanol derivatives for soft PVC was explored by means of calorimetric analysis in a broad range of compositions. Cardanol acetate was obtained by esterification of the cardanol hydroxyl group, and epoxidized cardanol acetate was obtained by further epoxidation of the side chain double bond. Differential scanning calorimetry was used to evaluate the limits of miscibility between the plasticizers and PVC. Hansen solubility parameter analysis was used to correlate the PVC-plasticizer miscibility to the chemical structure of the plasticizers. An environmental friendly, solvent-free innovative procedure was developed in order to obtain esterification in high yields, by the use of a new catalyst, zinc perchlorate hexahydrate [27,28]. Cardanol acetate was therefore used 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.

2. Materials and methods

The base polymer used was commercial PVC in powder form, Vestolit B7021 (Huls, Germany). The plasticizer was bis-(2-ethylhexyl) phthalate (DEHP) also from Huls. Technical cardanol, characterized by a purity of 95%, was purchased by Oltremare (Bologna, Italy). Zinc perchlorate hexahydrate was purchased by Aldrich Chemicals.

Esterification was performed by two different routes in order to produce cardanol acetate (CA). High purity, small scale esterification was performed in order to study the plasticizing effectiveness of the derived plasticizer, but let us produce no more than 7.5 g of plasticizer. This high purity esterification was obtained using, 7 g of cardanol and 6.57 ml (7.09 mol, 3 equivalents) of acetic anhydride, diluted in 5 ml di pyridine, and held for 2 h at 50 °C. Then, the solution was washed with HCl aqueous solution, dried, and filtered. Medium scale, batch esterification was also performed 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. Batch esterification was performed for 24 h at 25 °C without any purification.

Epoxidation was obtained mixing 10 g of cardanol acetate and 10.7 g (0.062 mol, 1.5 equivalents) of chloroperbenzoic acid in a flask, diluting with 1.3 l of dichloromethane, and holding for 3 h at 0 °C. The solution was washed with a water solution of Na_2CO_3, dried and filtered. The product obtained is epoxidized cardanol acetate (ECA).

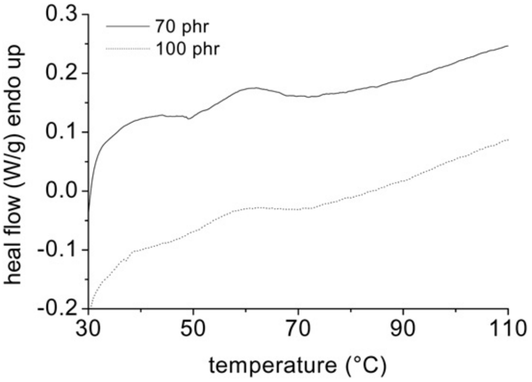


Fig. 2. DSC thermograms of soft PVC obtained with cardanol as primary plasticizer.

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

PVC plastisols were obtained by mixing PVC and the different plasticizers for 15 min at room temperature in a Haake Rheocord Mixer. Soft PVC was obtained by mixing PVC plastisols at 180 °C for 15 min in the same equipment.

Rheological analysis was performed on PVC plastisol in a Rheometrics Ares rheometer with a cone and plate geometry, at constant oscillatory amplitude (20%) and frequency (1 Hz), increasing the temperature at 5 °C/min to 170 °C, and then holding for 1 h.

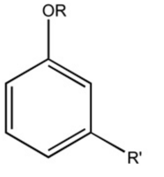
A simultaneous thermal analyzer Netzsch STA 409 was used for thermogravimetric (TGA) characterization, heating soft PVC samples from room temperature to 700 °C at 10 °C/min in air atmosphere.

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 °C–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.

For accelerated ageing test, circular samples about 2 mm thick and 40 cm in diameter were compression molded, and held at 105 °C at 50% relative humidity.



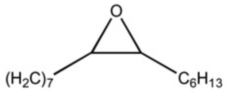
	R	R'
cardanol	H	$C_{15}H_{25-31}$
cardanol acetate (CA)	$COCH_3$	$C_{15}H_{25-31}$
epoxidated cardanol acetate (ECA)	$COCH_3$	

Fig. 1. chemical structure of cardanol and its derivatives.

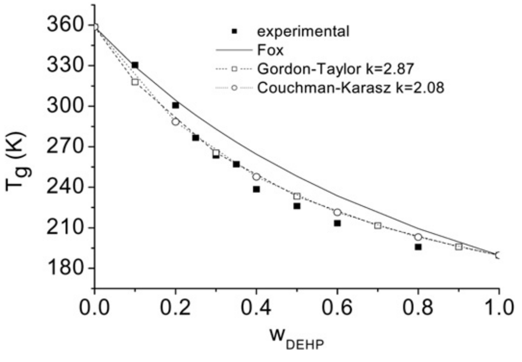


Fig. 3. T_g of soft PVC as a function of DEHP weight fraction.