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Effect of the epoxidation yield of a cardanol derivative on the plasticization and durability of soft PVC

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This work is aimed to the development and property optimization of cardanol derived plasticizers. To this purpose, different plasticizers were produced though different epoxidation routes, characterized by low toxicological and environmental impact. The plasticizers are characterized by different yield of epoxidation of the alkyl chain double bonds. The properties of the cardanol derived plasticizers were compared to the properties of commercial plasticizers, either phthalates or natural derived. Mechanical properties of soft PVC plasticized by cardanol derivatives were shown to be comparable to those of PVC with commercial plasticizers. The plasticizing efficiency of cardanol derivatives was significantly improved by increasing the yield of epoxidation. Also, mechanical properties performed after ageing showed the excellent stability of the properties of the cardanol derived plasticizer characterized by the higher yield. Evaluation of the property retention index after ageing indicated that such plasticizers showed an improved stability of properties compared to other commercial plasticizer. The results obtained highlight the relevance of an high conversion of the double bonds into epoxies in order to produce high quality plasticizers.

1. Introduction

In recent years, the use of phthalate plasticizers for the production of soft PVC has been subjected to severe revisions, due to their potential detrimental effects on human health [1,2] as well as to growing environmental awareness [3–5]. As a consequence, phthalate plasticizers were banned in different applications [6]. In addition, different indicators (eco toxicity, global warming) show that phthalate plasticizer production accounts for about 25–30% of the total life cycle impact of soft PVC [7].

The use of bio-plasticizers, derived from natural oil and properly modified to improve the compatibility with soft PVC, represents a valid alternative to phthalate plasticizers, aimed to reduce both the environmental and toxicological impact [8]. The main drawback associated to the use of bio-plasticizers is their high cost, which often is not compatible with the market price of soft PVC [8]. In addition, bio-plasticizes, derived from natural oil, contribute to the subtraction of resources to food chain, as is the case, for example, of epoxidized soybean oil [9].

On the other hand, the potential of cardanol derivatives as PVC plasticizers was demonstrated since the ’70 [10]. Cardanol is a natural resource, characterized by low cost and low toxicological impact, which nowadays finds uses in different chemical and polymer industries [11–13]. In addition, being a by-product of cashew nut shell industry, the cardanol derived plasticizers do not require the use of primary resources, and therefore do not contribute to the subtraction of resources to food chain.

In particular, it was shown that acetylation of the cardanol hydroxyl group improves the compatibility with PVC [14]. Therefore, cardanol acetate (CA) can be used as secondary plasticizer, in addition to conventional plasticizers, for the production of soft PVC. Nevertheless, the migration of CA is very high compared to the migration of conventional plasticizers [15]. Recently, it has been shown that also epoxidized cardanol glycidyl ether can be used as a secondary plasticizer, or at least as a primary plasticizer at very low contents (below 25 phr), for the production of soft PVC [16,17].

Other approaches used to reduce the migration of plasticizer from soft PVC include the use of cardanol derivatives covalently bonded to PVC; nevertheless, in this case, the plasticizing effectiveness of the plasticizer is significantly reduced, and addition of 160 phr of plasticizer leads to a reduction of the glass transition comparable to that obtained by addition of only 10 phr of DEHP

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[18].

Further epoxidation of cardanol acetate leads to the production of epoxidized cardanol acetate (ECA), a plasticizer characterized by a very good compatibility with PVC [15]. The main limitation in the production of ECA is the chemical modification of cardanol. In the most conventional reaction routes, esterification requires the use of acetic anhydride as reagent and pyridine as solvent, whereas epoxidation requires m-chloroperbenzoic acid as reagent and dichloromethane as solvent [13]. Such conditions are not suitable for the production of a green product. On the other hand, in a recent work [15,19] it has been shown that esterification can be performed by the use of acetic anhydride, in the presence of hexahydrate zinc perchlorate, without the use of solvents. Different attempts made to obtain epoxidation in similar solvent free conditions, characterized by low environmental and toxicological impact, showed a limited potentiality of the developed plasticizers, mainly due to the low degree of conversion of double bonds to epoxies [20]. Other epoxidized cardanol esters have been shown their potential as plasticizers for PVC. It was shown that a high yield of epoxidation promotes the formation of a soft PVC characterized by thermal properties comparable to those of soft PVC plasticized by DEHP, and e better plasticizer retention [19].

The aim of this work is the optimization of the properties of cardanol derived plasticizers by optimization of the procedure used for epoxidation. To this purpose, the properties of different plasticizers, characterized by different yield of epoxidation, were compared to the properties of commercial plasticizers, either phthalates or natural derived. In particular, a relevant part of the work is dedicated to the correlation between the functional properties of the plasticizer and the extent of epoxidation attained.

2. Materials and methods

The PVC used is Vestolit B7021 (Huls, Germany) in powder form. Cardanol derived plasticizers (CDP) were provided by Serichim (Torviscosa, Udine, Italy). All CDP were subjected to two reaction steps, esterification and epoxidation. Acetylation was performed by acetic anhydride (molar ratio 1.2:1), at 110 °C for 10 h, using Amberlyst 15, 3% weight as catalyst. Epoxidation was performed in different ways, with the aim of obtaining epoxidized cardanol acetate (ECA). All the reactions used hydrogen peroxide in order to obtain a peroxy acid by a proper catalyst system. Such reaction is an equilibrium reaction. The peroxy acid is the oxidizing agent, which is used in an uncatalysed reaction to obtain conversion of double bonds to epoxies. The second reaction is a quantitative reaction. The two reactions were tried in one-pot or in two-pot systems. In one pot system, all the reagents are fed in the same batch; in such case, it very important that the first reaction occurs before other side reactions, which can involve the direct and uncontrolled reaction between cardanol acetate, acid and catalyst. The main potential advantage of this system is that, when the peroxy-acid is consumed by the second reaction, the equilibrium of the first reaction is shifted to the formation of further peroxy-acid. In two-pot systems, the peroxy acid is formed in a first reactor, and then transferred in a second reactor, where cardanol acetate is fed and the second reaction occurs. The main advantage of this system is that the risk of side reactions in the second reactor is reduced, since the presence of the peroxy acid should involve a fast conversion of epoxies. In all the two-step reactions, the peroxy-acetic acid is obtained by mixing acetic acid and hydrogen peroxide (molar ratio 1:2) with Amberlist 15 resin catalyst (2.5% weight of the total batch weight); after 72 h at 30 °C the mixture is typically composed of 19% peroxy-acetic acid, 25% hydrogen peroxide, 15% acetic acid, 41% water. The following plasticizers were produced by one pot or two pot reactions:

- CDP27; one pot reaction. Cardanol acetate, hydrogen peroxide (1.5 mol to the moles of double bonds), acetic acid (15% to the total weight of the batch) and sulphuric acid catalyst (0.3% to the total weight of the batch) are charged in the 250 ml reactor with magnetic stirring; reaction was performed at 60 °C for 7 h;
- CDP54: two pot reaction. Cardanol acetate, peroxy-acetic acid (molar ratio to double bonds 1.4:1) and 10% toluene are charged in the reactor (magnetic stirring); reaction is run at 25 °C for 20 h;
- CDP81: two pot reaction. Cardanol acetate, peroxy-acetic acid (molar ratio to double bonds 1.4:1) are charged in the reactor (mechanical stirring at 480 rpm); reaction is run at 25 °C for 20 h.

The water phase (also including hydrogen peroxide and acetic anhydride) was removed by liquid-liquid centrifugal separation, whereas the acetic acid was removed by distillation under high vacuum (less than 10 torrs) at 70 °C.

Therefore, the developed procedures for epoxidation allowed to production of about 150 ml CDP. More recently, the process of epoxidation has been scaled up to the production of about 60 L of CDP, in a medium-scale industrial reactor [21].

According to the NMR analysis previously reported [22], each of the tested plasticizer is characterized by a certain yield of epoxidation, defined as the ratio between the number of epoxies formed on the alkyl side chain and the initial amount of double bonds, as reported in Table 1. The yield of epoxidation, is always lower than 100%, and therefore, the different CDP are actually composed of a mixture of cardanol acetate (CA), molecular weight $M_w = 342$ g/mole, epoxidized cardanol acetate (ECA), $M_w = 374$ g/mole, and side products of the epoxidation reaction, which are mainly composed of hydroxyl and carboxylic groups [23]. In particular, the presence of amounts of hydroxy-cardanol acetate is expected to negatively affect the performances of the plasticizer [22].

Epoxidized soybean oil (ESBO), $M_w = 1000$ g/mole, and Grindtsed soft-n-safe by Danisco, mainly constituted by fully acetylated glycerol monoester of 12-hydroxystearic acid (SNS), $M_w = 500$ g/mole, were provided by Kommi srl, Lequile, Lecce, Italy, while bis-(2-ethylhexyl) phthalate (DEHP), $M_w = 390$ g/mole, was given by Huls. Finally, PVC stabilizer (Reagens CL/123) and costabilizer (Reaflex EP/6) were kindly supplied by Reagens (Italy).

A preliminary estimation of the compatibility between the different plasticizers and soft PVC was obtained by evaluation of the interaction radius [14], based on the Hansen solubility parameter theory:

$$\delta = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5} \tag{1}$$

Where δ_d is the contribution of dispersion forces, δ_p is the contribution of permanent dipoles, and δ_h is the contribution of hydrogen bonding. By introducing a combination of dispersion and polar forces:

$$\delta_v = \left(\delta_d^2 + \delta_p^2\right)^{0.5} \tag{2}$$

The interaction radius IR was obtained as:

$$IR = \sqrt{\left(\delta_{v,PVC} - \delta_{v,plast}\right)^2 + \left(\delta_{h,PVC} - \delta_{h,plast}\right)^2} \tag{3}$$

The values of different terms contributing to the Hansen solubility parameters were calculated according to the additivity rule [24].

The values of the interaction radius estimated for cardanol derivatives and commercial plasticizers are reported in Fig. 1. The poor