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Material properties

Performance evaluation of new plasticizers for stretch PVC films

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ABSTRACT

Six stretch PVC films have been formulated to have Shore A hardness of approx. 80 and nominal thickness of 15 μm with the aim of evaluating the performance of plasticizers from renewable and non-renewable sources for stretch PVC films intended to be employed as packaging. The reference film was produced with DEHA and ESBO, while the other films were produced with conventional plasticizers (ATBC and Polyadipate), new plasticizers from renewable sources (Mixture of glycerin acetates and Acetic acid esters of mono- and diglycerides of fatty acids) or a plasticizer employed in toy and childcare applications (DEHT) as a third plasticizer. The films were evaluated as to their physical and mechanical properties (durometer hardness, tensile strength and elongation), IR spectroscopy and light transmission. The several plasticizers influenced the mechanical properties of the PVC films to different degrees. All films will probably show adequate performance when used in packaging applications. Nevertheless, the vegetable oil-based plasticizers showed better mechanical performance than the other plasticizers when compared to DEHA.

1. Introduction

Stretch PVC films are used to pack a broad variety of foodstuffs. These films have a large amount of additives (plasticizers). There are around three hundred chemical substances that may be used as PVC plasticizers and approximately one hundred which are of commercial importance. Of these commercially important primary plasticizers, esters are the most commonly known and used. Plasticizers are almost invariably esters because of their specific requirements for interacting with the polymer. Plasticizers in flexible PVC must be closely associated with the amorphous part of the polymer at room temperature, and plasticizers must be fairly permanent. The plasticizer must act as a solvent for the crystalline part of the PVC at flexible PVC processing temperatures but not at lower temperatures. Also, the plasticizer must not react with the PVC [1].

However, it is important to know the characteristics of the plasticizers for each intended application, such as their physical, chemical and toxicological properties. Phthalates play an important role in plastics and rubber around the world, accounting for more than 80% of all PVC plasticizers, and DEHP represents at least 60% of this amount due to its good performance and low price. Esters display variation in their molar mass and have been used for different applications for over 50 years thanks to their excellent properties and cost [1].

Some studies developed in the 90's showed that some plasticizers of the phthalate family caused genetic changes in mice, but that was not observed in humans. Anyway, the concept of precaution was placed on low-molar mass phthalates, such as BBP, DIBP, DIHP and DEHP, limiting their use in some products. On the other hand, high-molar mass phthalates such as DINP and DIDP do not have any restrictions to use [2,3].

Thus, some companies and sectors have looked for alternatives to certain phthalates, either voluntarily or

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compulsorily. As mentioned above, there are several alternatives, but many others have appeared, such as plasticizers of vegetable origin. These plasticizers also have a strong environmental appeal, since they are made from renewable resources. Examples of raw materials used are numerous, such as corn, soybean, sunflower, palm, castor bean and flaxseed, among others. Usually, the processes of transesterification, alkylation and epoxidation are used to manufacture these potential PVC plasticizers. The results have been quite promising and some markets are already trying and using them.

In accordance with this trend, the plasticizers from renewable sources, such as modified vegetable oil, modified and epoxidized vegetable oil, mixtures of glycerin acetates, glycerol monoester as well as di(2-ethylhexyl) terephthalate – DEHT are new alternatives for stretch PVC film applications.

The plasticizer fully acetylated monoglyceride based on hydrogenated castor oil (SNS) has been approved by European Union for food contact use without any restrictions. The plasticizer has no specific migration limit [4]. Migration studies of this plasticizer to acidic, alcoholic and fatty (sunflower oil) simulants have shown lower migration values than those observed for DEHP and DINP plasticizers, with a range of migration reductions from 50 to 100 times in aqueous simulants [5].

Another vegetable based plasticizer is the fully acetylated glycerol monoester based on coconut oil (Acetem) instead of castor oil used in SNS plasticizer. Hence, the main components of Acetem are caprylic (C8), capric (C10) and lauric acid (C12) while the main components of SNS are 12-hydroxystearic acid (85%) and stearic acid (C18 - 10%). Migration studies of the plasticizers SNS, Acetem and epoxidized soybean oil (ESBO) from PVC films into isooctane at different temperatures (20 °C, 40 °C and 60 °C) have shown that the diffusion coefficient of SNS is independent of temperature. Acetem has shown some correlation between the diffusion coefficient and the temperature, however this correlation does not obey the Arrhenius equation [6].

DEHT is a plasticizer made by ester linkage of two molecules of 2-ethylhexanol to terephthalic acid, being a structural isomer of di(2-ethylhexyl) phthalate – DEHP. However, DEHT is based on terephthalic acid that has two carboxylic acid groups at para position, while DEHP is based on phthalic acid that has two carboxylic acid groups at ortho position. This structural difference is very important since the toxicological profile of the effects of laboratory animals exposed to DEHT is significantly different from DEHP despite the isomeric relationship. The toxicological difference is related to the final metabolic products.

In vitro and *in vivo* metabolism studies have shown that DEHT is completely hydrolyzed at the two ester linkages since the two acid molecules are in opposite position to each other at the para position, allowing the complete metabolism. On the other hand, DEHP is partially hydrolyzed and the monoester metabolite produced is responsible for the induction of many toxicological effects associated with rodents exposed to DEHP. Due to this, study conducted with laboratory mice exposed to high concentrations of DEHT has shown minimum toxicity, reduced weight gain and possibly degenerative effects as significant toxicological effects being observed. Thus, the effect level observed in this study was considered as 1,500 ppm for systemic toxicity and 12,000 ppm for carcinogenicity [7]. Thereby, the plasticizer DEHT has European Food Safety Authority – EFSA approval for food contact with restriction of dairy ingestion tolerance – DIT of 1 mg/kg of body weight [8].

J-L Audic et al [9] investigated the compatibility of six thermoplastic elastomers with PVC with the aim of getting alternatives to DEHA plasticizer. According to the authors, a terpolymer of ethylene, vinyl acetate and carbon monoxide (EVACO) was shown to give the optimal properties for the processing of transparent, soft, PVC-based films. However, the incorporation of EVACO in the PVC formulation instead of DEHA represented an interesting compromise between migration and processability trade-off for PVC wrap films. A decrease of migration of the plasticizer DEHA by reducing its amount to zero was observed. On the other hand, the authors also observed an increase of the migration of ESBO, a toxicologically less prohibited additive. The prevention of the migration of the plasticizers makes possible the temporal stability of the film properties and, consequently, an improvement for customary usage.

Another approach to avoid migration of the plasticizer from the PVC to the product is attaching the plasticizer to the PVC chain through covalent bonds. According to Navarro et al. [10], good plasticization efficiency was achieved although flexibility was reduced compared with that of commercial PVC-phthalate systems. Nevertheless, the plasticizer migration was completely suppressed. This approach may open new ways to the preparation of flexible PVC with permanent plasticizer effect and zero migration, which is very important for food packaging applications.

The development of new PVC plasticizers is very important as well as evaluating the performance and the conformance of the packaging materials formulated with them with reference to the legislation in force. DEHA di(2-ethylhexyl) adipate), ESBO (epoxidized soybean oil), ATBC (acetylated tributyl citrate) and polymeric plasticizers are used in plastic packages for food (the last two plasticizers are used mainly in Europe due to their high cost) and are not hard to find in packages available in the market. Beside these plasticizers, new plasticizers from renewable sources and a plasticizer employed in toy and childcare applications - di(2-ethylhexyl) terephthalate – DEHT are being evaluated as plasticizers for stretch PVC films intended to come into contact with foodstuffs [6,7,11–13].

The aim of this study was to evaluate the performance of several plasticizers (from renewable and non-renewable sources) for stretch PVC films intended to be employed as packaging in order to get information for technical specification of these packages, besides knowledge about the performance of new plasticizers.

2. Experimental

2.1. Materials

The following PVC resin and plasticizers have been used in this study:

- PVC SP 1300 resin, K value 71 ± 1, supplied by Braskem S/A;