

Material properties

Performance evaluation of new plasticizers for stretch PVC films

Leda Coltro ^{a,*}, Joyce B. Pitta ^a, Emerson Madaleno ^b^a Packaging Technology Center – CETEA/ITAL, Av. Brasil, 2880, ZIP 13070-178 Campinas, SP, Brazil^b Braskem S.A. – Av. das Nações Unidas, 8501, 24° andar, ZIP 05425-070, SP, Brazil

ARTICLE INFO

Article history:

Received 5 October 2012

Accepted 19 November 2012

Keywords:

Polyvinyl chloride (PVC)

Film

Stretch

Plasticizer

Packaging

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.

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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

* Corresponding author. Tel.: +55 19 3743 1923.

E-mail address: ledacoltr@ital.sp.gov.br (L. Coltro).

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;

- Di(2-ethylhexyl) adipate - DEHA, density 0.924–0.929 g/cm³, supplied by Elekeiroz S/A;
- Epoxidized soybean oil - ESBO, Soyflex 6250™, density 0.987–0.993 g/cm³, molar mass 944 g/mol, supplied by BBC Indústria e Comércio Ltda.;
- Acetylated tributyl citrate - ATBC, Scandinol SP-22™, density 1.048 g/cm³, supplied by Scandiflex do Brasil S/A.;
- Mixture of glycerine acetates - Unimoll™ AGF, density 0.974 g/cm³, supplied by LANXESS Indústria de Produtos Químicos e Plásticos Ltda.;
- Di(2-ethylhexyl)-1,4-benzenedicarboxylate) - DEHT, Eastman 168™, molar mass 390.57 g/mol, density 0.983–0.988 g/cm³, supplied by Eastman Chemical Company;
- Acetic acid esters of mono- and diglycerides of fatty acids - GRINDSTED™ ACETEM 95 CO KOSHER (Acetic Acid Ester), molar mass 360 g/mole, density 0.98 g/cm³, supplied by Danisco Brasil Ltda.;
- Polyadipate - Plaxter P52™, molar mass approx. 2100 dalton, supplied by Coim Brasil Ltda.

The plasticizers were not purified prior to analysis.

2.2. Film preparation

Stretch PVC films with different plasticizer composition, 15 µm thickness on average, were produced for this study at Indústria Bandeirante de Plásticos Ltda. (Guarulhos, Brazil), in a commercial blowing machine operating at 25 rpm for 2 minutes at 170 °C. The plasticizer combinations are described below:

1. Sample 1 - DEHA + ESBO (reference)
2. Sample 2 - DEHA + ESBO + ATBC
3. Sample 3 - DEHA + ESBO + Mixture of glycerine acetates
4. Sample 4 - DEHA + ESBO + DEHT
5. Sample 5 - DEHA + ESBO + Acetic acid esters of mono- and diglycerides of fatty acids
6. Sample 6 - DEHA + ESBO + Polyadipate

The composition of the films is shown in Table 1. These formulations were selected in order to get approximately 80 Shore A hardness.

Sample 1 was adopted as reference to rate performance of the stretch PVC films as to mechanical properties, since this sample was produced with the most commonly used plasticizers in the Brazilian market - DEHA and ESBO.

Table 1
Formulations of the stretch PVC films evaluated.

Component	Sample 1 (%)	Samples 2-5 (%)	Sample 6 (%)
PVC K71	71.1	71.1	67.3
ESBO	5.7	5.7	5.4
Other additives	2.6	2.6	2.4
DEHA	20.6	1.4	6.7
3rd Plasticizer	0.0	19.2	18.2
Total plasticizers	26.3	26.3	30.3

2.3. Film characterization

In order to characterize and to evaluate the efficiency of the plasticizers in stretch PVC films for packaging the following methods were employed: physical mechanical properties, infrared spectroscopy and light transmission. The tests were conducted at 23 °C ± 2 °C and 50% ± 5% relative humidity after conditioning the samples in these same conditions for at least 48 hours.

2.3.1. Shore test

The Shore A durometer hardness of the samples was determined according to ASTM D2240 [14]. 8-cm diameter and 3-mm thick cylindrical specimens were evaluated in a Bareiss GmbH durometer hardness, model BS61 Shore A. Five measures at 15 s per film formulation were performed.

2.3.2. Density

The density of the samples was determined by displacement according to ASTM D792-08 [15]. Five measures per film formulation were performed.

2.3.3. Thickness

Thickness of the films was measured by mechanical scanning according to ISO 4593 [16]. A digital indicator ID-H Series 543 (Mitutoyo, Japan), 0.1 µm resolution was used. Measurements were taken at 25 different positions of the film surface and the mean value is reported.

2.3.4. Tensile properties

The tensile properties of the samples were determined according to ASTM D882-10 [17]. 25.4-mm wide specimens were assessed in an Instron universal machine, model 5500R, operating with a 50 N load cell, at a speed of 500 mm/min. The initial distance between the grips was 50 mm. The tensile strength was expressed as the maximum force at break divided by the initial cross-sectional area of the film specimen, and the elongation at break as a percentage of the original length.

2.3.5. Infrared spectroscopy

The samples were identified using Fourier transform infrared spectroscopy in a Perkin Elmer equipment model Spectrum 100. The infrared spectra were obtained based on ASTM E 1252-98 (2007) [18] standard practice for general techniques to get infrared spectra for qualitative analysis. The samples of plasticizers were identified with a potassium bromide window (KBr), whereas samples of plastic films were identified by direct reading. The spectra were obtained in duplicate at 450–4000 cm⁻¹ using a resolution of 1 cm⁻¹.

2.3.6. Light transmission

Regular light transmission analysis was performed on a Specord 210 UV-Visible spectrophotometer, from Analytik Jena. The spectra were registered at a scanning rate of 120 nm/min, from 200 to 800 nm. Three specimens per sample were obtained from different regions of the films [19].

2.4. Statistical analysis

Analysis of variance was applied to the results and Fisher's least significant difference (LSD) test was used to

determine statistically significant differences ($p < 0.05$) between averages using Software Statgraphics Plus 5.0 (swing).

3. Results and discussion

3.1. Mechanical properties

The Shore hardness results are a useful measure of relative resistance to indentation of various grades of polymers. Shore A scale is the preferred method for softer plastics such as polyolefins, vinyls and fluoropolymers. Although these results cannot be used to predict other properties such as strength of the polymers, they are commonly used as a mechanical performance parameter. According to the results shown in Table 2, PVC films showed 5–10% higher hardness than sample 1 (reference).

According to the free volume theory of plasticization, motions in the plasticizer molecule added to the polymer create free volume in the polymer matrix. Free volume is the space between molecules and it is defined as the difference in specific volume at some temperature and a reference temperature, usually absolute zero. Free volume in the polymer could come from several sources, such as motion of polymer end groups, motion of polymer side groups as well as internal polymer motions [1]. Then, the plasticization efficiency depends on the degree of free volume increase in the PVC matrix. The higher the free volume, the higher the PVC flexibility.

PVC hardness depends on the plasticizer concentration, the higher the plasticizer efficiency the lower plasticizer concentration. The plasticizers evaluated in this study have shown lower plasticization efficiency than DEHA since the plasticizers were applied at approximately 19% in all the PVC samples formulation and all of them showed higher hardness than sample 1. However, samples 3 and 5 showed a lower hardness increase than the others, so both vegetable oil-based plasticizers used in these samples have shown better plasticization efficiency than the other plasticizers evaluated.

The density of the materials depends on their crystallinity, as well as their composition (types or proportions of resin, additive, pigment or filler). Since all the second main plasticizers used have similar density and their proportion in the composition of the PVC films are also similar, except by the film with polymeric plasticizer, then the increase in the density of the films in relation to the reference sample 1 probably is related to the molecular interactions between the polar parts of the plasticizer

molecules (e.g. aromatic ring, ester linkages, glycerol) and the PVC resin via van der Waals forces and dipole-dipole interactions.

Tensile strength of films depends on the resin and additives used in their composition, i.e. the material itself. Hence, this property along with elongation at break is a good way to evaluate the efficiency of plasticizers.

The results of the tensile properties in the machine direction of the stretch PVC films are shown in Table 3. Except for sample 3, all the other samples showed significantly higher tensile strength than reference sample 1, with 95% confidence (LSD test). Samples 2, 4 and 6 showed the highest values (increase ranged from 40% to 50%), with no significant differences between them, i.e. the films produced with monomeric (ATBC and DEHT) and polymeric (polyadipate) plasticizers showed lower plasticization efficiency than the reference (DEHA) since all samples have the same amount of the main plasticizer (approx. 19%).

Although film 6 has been produced with higher amount of total plasticizers (approx. 30%), this sample showed less plasticization efficiency than DEHA due to the lower efficiency of the polyadipate to interact with and to plasticize PVC compared to the other plasticizers evaluated.

Therefore, the plasticizers of the samples 2, 4 and 6 should be added at higher amount in the PVC film composition in order to get the same tensile strength as the reference sample. However, this can be a problem if the PVC film is intended to come into contact with foodstuffs since plasticizers added in high amount can migrate to the packed food.

On the other hand, sample 3 produced with vegetable oil-based plasticizer (mixture of acetylated glycerides) showed the same plasticization efficiency as DEHA, while sample 5, also produced with vegetable oil-based plasticizer (acetic acid esters of mono- and diglycerides of fatty acids), showed the same performance as sample 3 (no significant difference with 95% confidence, LSD test). Therefore, at the same composition in PVC films only the vegetable oil-based plasticizers showed tensile strength similar to the reference film, probably due to higher interaction between the polymer chain and the chemical structure of these plasticizers, promoting greater distance between the polymer chains [1].

Both vegetable oil-based plasticizers evaluated in this study showed plasticizer properties similar to the natural

Table 2
Physical characterization of the stretch PVC films evaluated.*

Sample	Shore A Hardness	Density (g/cm ³)
1	83.2 ± 0.1	1.239 ± 0.001
2	89.6 ± 0.1	1.290 ± 0.001
3	87.7 ± 0.3	1.268 ± 0.001
4	91.2 ± 0.4	1.272 ± 0.001
5	87.9 ± 0.3	1.270 ± 0.001
6	91.4 ± 0.5	1.312 ± 0.001

*Average ± standard deviation of 5 experimental determinations.

Table 3
Mechanical properties of the stretch PVC films evaluated (machine direction).

Sample	Thickness (μm)*	Tensile strength (MPa)**	Elongation at break (%)**
1 (ref.)	16 ± 1.6 ^b	24.5 ± 2.9 ^a	227 ± 38 ^a
2	15 ± 1.0 ^a	36.8 ± 5.6 ^c	202 ± 36 ^{ab}
3	17 ± 0.9 ^c	27.2 ± 2.1 ^{ab}	194 ± 27 ^b
4	19 ± 1.4 ^d	34.5 ± 2.2 ^c	190 ± 26 ^b
5	18 ± 1.0 ^d	29.6 ± 3.2 ^b	192 ± 27 ^b
6	20 ± 0.8 ^e	34.1 ± 5.5 ^c	200 ± 27 ^{ab}

*Average ± standard deviation of 25 experimental determinations.

**Average ± standard deviation of 10 experimental determinations.

Different letters in the same column indicate significant differences ($p < 0.05$).

polymeric plasticizer obtained through polyesterification of rice fatty acid evaluated by Silva et al. [15]. These authors found tensile strength in the range 22 to 27 MPa using 30% of plasticizer in the film composition, while in the present study approximately 26% of total plasticizers was used.

Although samples 2 and 6 showed tensile strength 40–50% higher than the reference sample, the elongation at break of these samples did not differ significantly from the reference sample. All the other samples showed 15% lower elongation at break values.

All the samples showed elongation of approximately 200% at break. Samples 3, 4 and 5 showed 15% lower elongation than sample 1 (reference), with 95% confidence (LSD test). This performance is the most important in the use phase of stretch PVC films when wrapping trays, fruits etc., being stretched by the user to wrap the product.

These diverse tensile properties of the samples are due to the chemical characteristics of the plasticizer used in PVC films, since the relative concentration of plasticizers in the film formulations was kept constant.

According to the results, all the samples evaluated will probably show adequate performance when the stretch PVC films are used in packaging applications.

3.2. Infrared spectroscopy

FTIR methods typically look at the PVC resin carbon-chlorine bond and plasticizer groups (carbonyl when the plasticizer is an ester, or epoxy when it is an epoxidized oil etc.)

FTIR spectra of the plasticizers and the PVC film samples were obtained. The main absorption bands in the infrared

are shown in Table 4. The FTIR spectra for PVC films showed characteristic peaks of this polymer (Fig. 1): C–H bond stretching at 2900 cm^{-1} , $\text{CH}_2\text{--Cl}$ angular deformation at 1426 cm^{-1} , CH_3 and CH_2 groups deformation at 1380 and 1335 cm^{-1} , Cl–CH out of plane angular deformation at 1255 cm^{-1} , out of plane trans deformation at 960 cm^{-1} and C–Cl bond stretching at 833 , 694 and 615 cm^{-1} . These bands are in accordance with data found in literature for PVC [20–22].

FTIR spectra of the stretch PVC films showed, besides the characteristic peaks for the PVC, bands characteristics of the plasticizers:

- Sample 1: bands at 1739 cm^{-1} , 1463 cm^{-1} , 1255 cm^{-1} (most intense) and 1178 cm^{-1} corresponding to C=O and C–O–C vibration modes;
- Sample 2: bands at 1741 cm^{-1} , 1465 cm^{-1} , 1255 cm^{-1} (most intense) and 1186 cm^{-1} due to C=O, saturated aliphatic ester and C–O–C vibration modes;
- Samples 3 and 5: bands at 1744 cm^{-1} , 1370 cm^{-1} , 1228 cm^{-1} (most intense), 1102 cm^{-1} and 1051 cm^{-1} corresponding to C=O, aliphatic esters and C–H vibration modes;

Table 4
Main infrared absorption bands of the plasticizers and PVC films.

Wavelength (cm^{-1})	Functional group	Vibration mode
2960	CH_3	Asymmetric stretching
2930	CH_2	Asymmetric stretching
2872	CH_3	Symmetric stretching
2855	CH_2	Symmetric stretching
1730	C=O	Stretching
1600	C=C aromatic	Stretching
1580	C=C aromatic	Stretching
1462 and 1175	C–O–C	Stretching
1426	$\text{CH}_2\text{--Cl}$	Angular deformation
1380	CH_3	Symmetric angular deformation
1335	CH_2	Angular deformation
1255	Cl–CH	Out of plane angular deformation
1270 and 1118	C–H aromatic	In plane angular deformation
1074	C–H or C–C aromatic	In plane angular deformation
960	C–H	Out of plane trans deformation
835	C–Cl	Stretching
732	C–H aromatic 1,4 bi-substituted	Out of plane angular deformation
694	C–Cl	Stretching
635	C–Cl	Stretching

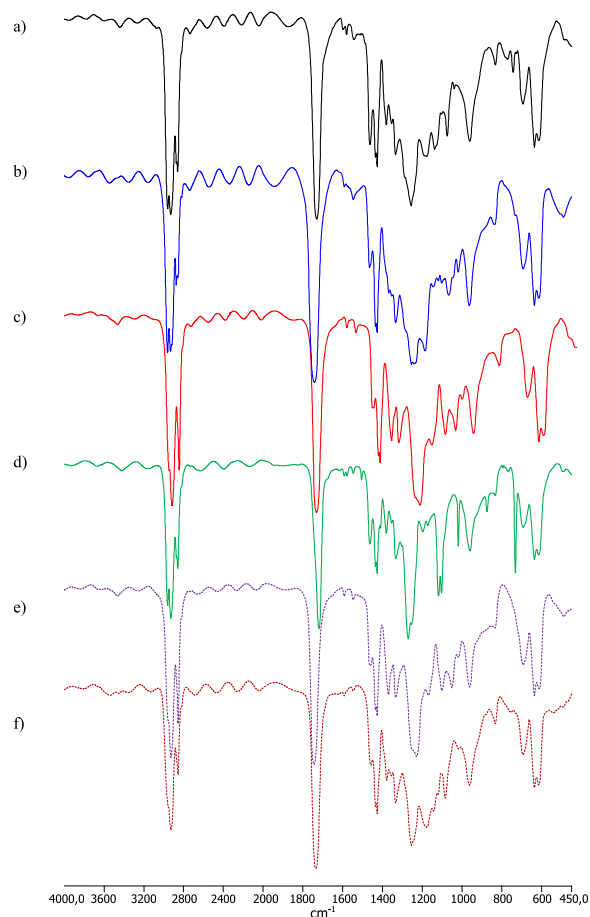


Fig. 1. FTIR spectra of PVC films prepared with different plasticizers: a) sample 1, b) sample 2, c) sample 3, d) sample 4, e) sample 5 and f) sample 6.

- Sample 4: bands at 1718 cm^{-1} , 1270 cm^{-1} (most intense), 1118 cm^{-1} , 1019 cm^{-1} and 732 cm^{-1} due to C=O, ester of aromatic acids and C–H aromatic vibration modes;
- Sample 6: band at 1734 cm^{-1} , 1255 cm^{-1} , 1177 cm^{-1} and 1084 cm^{-1} due to C=O, aliphatic ester and C–H vibration modes.

The carbonyl group absorption frequencies of the ester plasticizers can be shifted to frequencies several wave numbers lower (lower energy) when the ester group interacts with the PVC [1]. This band shift was observed for samples 3 and 5 (displacement of 4 cm^{-1} lower), indicating higher interaction between the plasticizers and the PVC resin than samples 2, 4 and 6 (shift of 4 cm^{-1} higher) as shown in Fig. 1. The intermolecular interaction between the polar parts of the plasticizer (carbonyl group) and the PVC (carbon-chloride bond) weakens the intramolecular bonding forces of the PVC polar groups, which is consistent with the lower tensile strength of samples 3 and 5 than samples 2, 4 and 6 (Table 3).

3.3. Light transmission

Fig. 2 shows the regular light transmission spectra for stretch PVC films produced with different plasticizer formulations. Samples 2, 3, 5 and 6 showed high transparency (%T approx. 90%) both in the UV region (wavelength lower than 380 nm) and visible region (wavelength higher than 380 nm).

However, samples 1 and 4 showed lower light transmission below 300 nm. Since all samples have the same amount of plasticizer, this different light transmission probably is due to the type of plasticizer used in the film formulation.

Sample 4 shows light barrier at wavelengths below 300 nm, probably due to the terephthalic group of the plasticizer since polyethylene terephthalate - PET also shows light barrier below 300 nm [23,24].

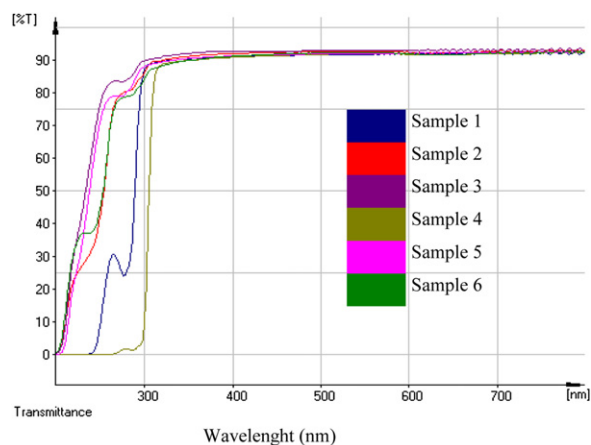


Fig. 2. Regular light transmission spectra of stretch PVC films with different plasticizer types.

3.4. Next steps

The PVC films assessed in this study are being evaluated in relation to overall migration to acidic and fatty food simulants, as well as to plasticizer specific migration for those that have migration limits established by legislation for food contact material and to investigate the presence of eventual off flavors.

4. Conclusions

Considering the tensile properties, all samples will probably show adequate performance when used as stretch PVC films with slight differences between them as follows:

- The plasticizer mixture of glycerine acetates showed the same plasticization efficiency as DEHA;
- The plasticizer acetic acid esters of mono- and diglycerides of fatty acids showed the same plasticization efficiency as the mixture of glycerine acetates but lower efficiency than DEHA;
- The plasticizers ATBC, DEHT and polyadipate showed lower plasticization efficiency than the others since samples 2, 4 and 6 showed the highest tensile strength values.

The vegetable oil-based plasticizers showed better mechanical performance (values similar/near to DEHA) than the other plasticizers evaluated.

The infrared spectra of PVC films can indicate the class of plasticizer used in the formulation as well as the strength of the plasticizer-PVC interactions.

Sample 4 showed light barrier at wavelengths below 300 nm, probably due to the terephthalic group of the plasticizer - DEHT.

Acknowledgements

The authors are grateful to FAPESP, Bandeirante, Braskem, BBC, Coim, Danisco, Eastman, Elekeiroz, Lanxess, Scandiflex for the financial support and the samples provided. The authors also thank CETEA's technical staff for collaborating with the tests.

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