

Migration of Additives from Food Grade Polyvinyl Chloride (PVC) Films: Effect of Plasticization by Polymeric Modifiers Instead of Conventional Plasticizers

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ABSTRACT: Based on the static and dynamic mechanical properties of the corresponding blends, the compatibility of six thermoplastic elastomers with polyvinyl chloride (PVC) was investigated. 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. FTIR spectroscopic analysis of EVACO plasticized blends clearly shows that the interactions involve the carbonyl groups of the VA and not of the CO monomer units. The migration phenomenon was studied on PVC based samples plasticized with di-2-ethylhexyladipate (DEHA) and EVACO in varying amounts. The overall migration (OM) was monitored by the weight loss percentage

of the samples immersed into isooctane at 40°C. The specific migrations of DEHA (SM_D) and epoxidized soybean oil (SM_E) were shown to be responsible for the overall migration ($OM = SM_D + SM_E$). The weight percentages of DEHA and epoxidized soybean oil (ESO) were correlated to the excess of immersion temperature (40°C) over the varying glass transition temperature of the samples. The results are explained with respect to the plasticizing effect of the additives and to the permanency of the EVACO-plasticization. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1291–1299, 2003

Key words: polyvinyl chloride (PVC); plastics; FTIR; block copolymers; blends

INTRODUCTION

In order to protect consumers from the contamination of foodstuffs and to improve the permanence of the polymer properties, the migration of additives, especially plasticizers from polymeric materials into food simulants, has raised many concerns.^{1–7} These concerns cover experimental evaluation, legislation and theoretical prediction. Beyond many other applications, plasticized polyvinyl chloride (PVC) is widely used as wrap film for food packaging. These PVC-based films usually contain plasticizers and coplasticizers such as di-2-ethylhexyladipate (DEHA) and epoxidized soybean oil (ESO), respectively. Surface modification techniques were shown to be efficient in preventing the migration of these PVC additives into food simulants. Typically, no plasticizers migrated from surface modified flexible PVC sheets after chemically induced⁸ and plasma induced⁹ surface crosslinkings while, under the same conditions, unmodified PVC lost almost all its plasticizers. However, these surface modifications led to significant decreases in the required mechanical and optical properties for

the use in food packaging. Therefore we have considered the use of polymeric modifiers (PM) instead of low molar weight plasticizers^{9–13} as a reasonable alternative to surface modification techniques.

Based on their known compatibility with PVC, several commercial polymeric modifiers (PM) were selected. For each PM, two compositions were designed, one containing both DEHA and PM (F_1) and the other containing only PM in total replacement of DEHA (F_2). Referring to their mechanical properties, these blends were compared with a conventional DEHA-plasticized PVC blend (F_0), which corresponds to a typical formulation in the manufacture of PVC wrap film. Based upon the best stress–strain curves and legislative requirements for food packaging, a terpolymer of ethylene, vinyl acetate and carbon monoxide (EVACO) was shown to be the best, most convenient PM. The plasticizing effect of EVACO was followed by dynamic mechanical thermal analysis (DMTA) of F_2 blends containing increasing amounts of EVACO. Polymer–polymer interactions were addressed by submitting blends of EVACO with varying amounts of PVC to FTIR analysis. Finally, the migration phenomena of (i) DEHA-plasticized PVC, (ii) EVACO- and DEHA-coplasticized PVC, and (iii) EVACO-plasticized PVC were compared. The overall migration (OM), and the specific migrations (SM_D) and (SM_E) of DEHA and ESO, respectively, were determined in isooctane at 40°C.

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EXPERIMENTAL

Materials

THF (Acros, Geel, Belgium, 99.5 + %), isooctane (2,2,4-trimethylpentane, Acros, purity >99.5%), di-2-ethylhexylphtalate (DEHP, Acros, purity >99%), were used as received.

PVC-based dry blends with varying contents of di-2-ethylhexyladipate (DEHA) were supplied by LinPac Plastics (Pontivity, France). The weights per hundred parts of resin (phr) (suspension PVC with K value of 70) were unvarying for epoxydized soybean oil (ESO: 10 phr), metal stearates (0.88 phr), glycerol monooleate (GMO: 0.8 phr) and trisnonylphenyl phosphite (TNPP: 0.16 phr). Polymeric modifiers were commercial elastomers. PCL/TPU (Estane 54351, Mw = 293100, Ip = 2.6) and PE/TPU (Estane 58213, Mw = 106500, Ip = 2.3) were both supplied by Goodrich (Brussels, Belgium). They are both polycaprolactone glycol-based thermoplastic urethanes, but PE/TPU has an additional poly(tetramethylene ether) glycol as a soft block and some of the concerned glycols are polyadipates. PE/TPBT is a polyether-based thermoplastic terephthalate (Hytrel 3548L, DuPont, Geneva, Switzerland). EVACOh and EVACO are two grades of poly(ethylene-co-vinyl acetate-co-carbon monoxide), respectively Elvaloy 741 (Hardness shore A: 70, Mw = 254400, Ip = 7.3) and Elvaloy 742 (Hardness shore A: 55, Mw = 240200, Ip = 6.5), both supplied by Du Pont. EBACO is a poly(ethylene-co-butyl acrylate-co-carbon monoxide) (Elvaloy HP661, Du Pont, Mw = 285300, Ip = 5.6). All of the polymeric modifiers were used as received.

Melt mixing

Blends were melt-mixed using a RHEOMIX HAAKE internal mixer. The fill factor in the chamber was around 0.7, and mixing was carried out at 180°C and 60 rpm rotor speed until torque stabilization (7-8 min). In the case of PVC/elastomer blends (100 : 60), the polymeric modifier is usually incorporated two times. Half is incorporated at the beginning of the mixing in a salt and pepper blend of pellets in PVC powder, and the second half is incorporated after 4 min. Compression molded plaques were prepared from the compounded stocks at 170°C.

Stress-strain testing

Uniaxial stress-strain and ultimate properties were performed using a LLOYD Instrument testing machine, M 30 K model, employing a crosshead speed of 50 mm/min. Samples were cut from 2 mm thick compression molded sheets by using an ASTM D 638 die (115 × 6 × 2 mm).

Hardness Shore A and Shore D were performed on ATS-FAAR type A and D testers.

Migration tests

Migration tests were performed on 14 cm² × 80 μm solution cast films obtained by solvent evaporation. THF solutions containing the PVC compounds and polymeric modifier (if present) were mixed and the solvent was evaporated at room temperature. The resulting PVC film was weighed (125 mg < w₀ < 135 mg) and immersed in 50 ml of isooctane at 40°C, without stirring, for two hours. The film was rinsed with isooctane, dried at 110°C for 20 min and weighed (w₁). The isooctane solution was evaporated and the resulting residue was dried for 24 h at 110°C. The weights of DEHA (w_A) and ESO (w_E) in the residue were determined by supercritical fluid chromatography (SFC) as described in a previous paper.⁹

The overall migration was determined from the weight loss ($\Delta w = w_0 - w_1$) of the PVC film and expressed in terms of percentage with respect to the weight (w₀) of the starting PVC film using the following equation: OM = ($\Delta w/w_0$)%.

The specific migrations of DEHA (SM_D) and ESO (SM_E) were expressed in terms of percentage with respect to the weight w₀ of the starting PVC film: SM_D = (w_{A1}/w₀)% SM_E = (w_{E1}/w₀)%

Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were carried out on a Rheometric Scientific MK III. Samples of 2 mm × 6 mm were initially cooled at -100°C and the measurement of the dynamic storage (E') and loss (E'') as well as the resulting tan δ (E'/E'') were conducted at 1 Hz in clamp binding mode with a heating rate of 10°C/min.

Fourier transformed Infra-red (FTIR) analysis

FTIR spectra (4000–600 cm⁻¹) were obtained on a Bruker IFS 66 spectrometer with a high-resolution nitrogen cooled MCT detector. Blends of PVC with EVACO were prepared in solution with tetrahydrofuran (THF) as the solvent at appropriate concentrations of PVC and EVACO to obtain 100 : 0, 80 : 20, 60 : 40, 40 : 60 and 20 : 80 by weight EVACO : PVC ratios. The film forming formulation was then spread onto a glass plate, and, after the excess solvent was eliminated by evaporation, the film was peeled off, dried and stored at room temperature. The samples were submitted to infrared spectroscopy with two hundred scans at a resolution of 1 cm⁻¹. The signal-averaged spectra were stored on a magnetic disc system.

TABLE I
Typical Properties of Selected Polymeric Modifiers

Polymeric Modifier (PM)	PE/TPU	PCL/TPU	PE/TPBT	EVACOh	EVACO	EBACO
Density (g/cm ⁻³)	1.18	1.16	1.15	1	1.02	0.98
Test Method	DIN 53479	DIN 53479	ASTM D 792	ASTM D 792	ASTM D 792	ASTM D 792
Stress at Break (MPa)	25	42	10.3	5.9	4.2	5.3
Test Method	DIN 53504	DIN 53504	ASTM D 638	ASTM D 1708	ASTM D 1708	ASTM D 1708
Strain at Break (%)	700	530	200	959	1200	1400
Test Method	DIN 53504	DIN 53504	ASTM D 638	ASTM D 1708	ASTM D 1708	ASTM D 1708
Hardness (shore A or D)	76 A	84 A	35 D	70 A	55 A	56 A
Test Method	DIN 53505	DIN 53505	ASTM D 2240	ASTM D 2240	ASTM D 2240	ASTM D 2240
T _g (°C) ^a	-38	-32	-28	-24	-25	-38

^a Determined by DSC.

RESULTS AND DISCUSSION

Selection of polymeric modifiers

Decreased migration caused by reduced plasticizer content in the starting PVC-based formulation necessitates the addition of a PVC miscible polymeric modifier (PM) to compensate for the loss in plasticity. Plasticization via incorporation of PM into PVC requires this PM to be completely miscible with PVC and to present a low temperature of glass conversion (T_g). Indeed, the incorporation of PM with low T_g values into PVC-based formulation has resulted in the formation of soft materials without the addition of liquid plasticizers.¹²⁻¹³ Based on the specific interaction between the carbonyl groups and the alkyl chloride groups and the resulting net exothermic heat evolved by mixing PVC with miscible polycaprolactone (PCL),¹⁴⁻¹⁵ thermoplastics containing PCL or PCL-like polyester as soft segments have been selected for the study. Such polyurethane-based (TPU)¹⁶ and polyether-based (PE/TPBT)¹⁷ thermoplastics were shown to be compatible with PVC. For the same reason, copolymers of ethylene with vinyl acetate and alkyl acrylates were also selected for this work. In this field, terpolymers of ethylene, vinyl acetate and carbon monoxide (EVACO) gave better results¹⁸ than EVA copolymers.¹⁹ It was shown that good miscibility with PVC can be reached for high concentrations of ethylene in EVACOs terpolymers. The carbon monoxide incorporation decreases the level of polyethylene crystallinity and is expected to favor a specific interaction holding the PVC and EVA molecules together through carbon monoxide units. In the same way, carbon monoxide incorporation in ethylene butyl acrylate copolymers was shown to enhance miscibility with PVC and allows high PE tenor.²⁰

In this context, six possible polymeric modifiers to be incorporated in PVC-based formulations for processing into flexible films were obtained from commercial sources: two polycaprolactone-based TPU, one containing an additional poly(tetramethylene ether) glycol as a soft segment (PE/TPU) and one

without (PCL/TPU), one polyether-based polyterephthalate thermoplastic (PE/TPBT), two EVACO terpolymers (EVACOh and EVACO) and one terpolymer of ethylene, butyl acrylate and carbon monoxide (EBACO). Table I shows their mechanical and thermal properties.

All of the six PMs, used in the form of pellets or granules, are high molecular weight solids. As indicated in Table I, they are soft compounds of low Shore A or D hardness with low T_g values (-24°C), low tensile strength and high elongation at break (more than 900% for EE-based terpolymers).

Optical, thermal and Stress-strain properties of initially selected PMs

The first aim of this study was to analyze the properties of a standard formulation (F_0) characterized by a PVC : ESO : DEHA : PM weight ratio of 100 : 10 : 28 : 00. F_0 samples were colorless and transparent, with a T_g value of 51°C . Such samples present high elongation at break (150–200 %), low elastic modulus (20–30 MPa) and hardness between 70 A and 85 A. For each PM, two PM-based formulations, F_1 and F_2 , characterized by PVC : ESO : DEHA : PM weight ratios of 100 : 10 : 10 : 40 and 100 : 10 : 0 : 60, respectively, were prepared. The optical, thermal and stress-strain properties of the corresponding blends were tested and compared with those of the F_0 sample and those of two PM-free samples, $F_{1/0}$ and $F_{2/0}$ characterized by PVC : ESO : DEHA : PM weight ratios 100 : 10 : 10 : 00 and 100 : 10 : 00 : 00, respectively. The numerical values of these tests are listed in Table II.

All the PM-based samples were colorless and showed good optical transparency. Moreover, for all of them, the mechanical loss curves obtained by dynamic mechanical thermal analysis (DMTA) in the (-100°C)–($+100^\circ\text{C}$) temperature range, exhibit only one typical loss peak, corresponding to the T_g . As expected, the T_g values fall between the T_g of the concerned PM and the T_g of the PM-free samples, $F_{1/0}$ and $F_{2/0}$ (Table II). These results agree with the mis-

TABLE II
Physical Properties of PVC-Polymeric Modifier Blends.

Polymeric Modifier (PM)	Sample	PVC/ESO/DEHA/PM Weight Ratio	Stress at 100% (MPa)	Stress at Break (MPa)	Elongation at Break (%)	Elastic Modulus (MPa)	Hardness (Shore A or D)	T_g ($^{\circ}\text{C}$)
None	F ₀	100/10/28/00	15.3	20.0	167	24.1	79 A	51
None	F _{1/0}	100/10/10/00	—	25.9	68	279.5	63 D	71
None	F _{2/0}	100/10/00/00	—	33.2	8.5	1110	75 D	82
PE/TPU	F ₁	100/10/10/40	15.4	23.4	188	42.9	85 A	52
	F ₂	100/10/00/60	16.9	29.4	248	104	88 A	57
PCL/TPU	F ₁	100/10/10/40	17.4	24.4	183	53.3	85 A	56
	F ₂	100/10/00/60	19.3	30.5	201	110.6	89 A	58
PE/TPBT	F ₁	100/10/10/40	16.9	24.1	197	55.2	83 A	51
	F ₂	100/10/00/60	17.9	27.4	215	102	86 A	56
EVACOh	F ₁	100/10/10/40	12.9	19.9	201	22.7	78 A	38
	F ₂	100/10/00/60	12.9	22.7	228	22.8	81 A	41
EVACO	F ₁	100/10/10/40	12.2	19.3	201	17.2	79 A	37
	F ₂	100/10/00/60	11.1	20.5	243	14.7	81 A	41
EBACO	F ₁	100/10/10/40	11	19.3	233	14.7	77 A	31
	F ₂	100/10/00/60	9.7	19.1	270	13.7	76 A	35

cibility of the blend components.²¹⁻²² It should be noted that, while the EVACOs exhibit higher T_g values than the TPEs (PCL/TPU, PE/TPU and PE/TPBT) (Table I), the EVACO-based PVC blends exhibit lower T_g values than the TPE-based blends (Table II). However, the T_g values of the F₁ samples containing DEHA are systematically lower than the T_g values of the F₂ samples. These observations show the promise of EVACO and of DEHA-EVACO mixtures in the plasticization of PVC.

The loss in the elastomeric properties induced by decreasing the plasticizer content is illustrated by the high values of the elastic modulus and hardness of F_{1/0} and F_{2/0} samples (Table II). The effectiveness of PM addition is clearly shown by the net corresponding slowdown of both elastic modulus and hardness. However, comparing the TPEs and the EE-based terpolymers, noticeable differences appear in the tendency to reach the targeted F₀-like properties.

Figures 1 and 2 show the stress-strain curves for F₁ and F₂ samples respectively, as a function of the PM

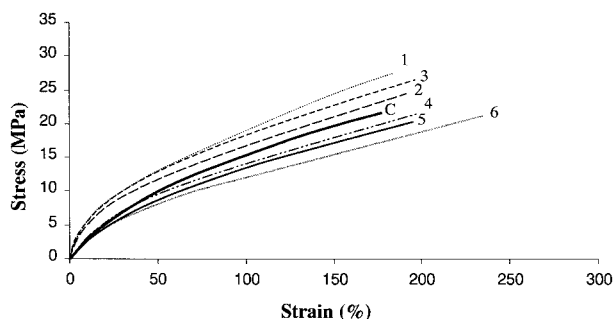


Figure 1 Stress-strain curves for F₁ samples as a function of polymeric modifier (PM): (1) PCL/TPU, (2) PE/TPU, (3) PE/TPBT, (4) EVACOh, (5) EVACO, (6) EBACO, (C) F₀ control sample.

used. In each case, the curve corresponding to the F₀ sample is given as a reference. It can be noted that, for each PM, elongation at break is always higher than for the F₀ sample and that this improvement is more accentuated for F₂ samples (Figure 2), which do not contain DEHA, than for F₁ samples (Figure 1), which contain DEHA. This observation is an additional point of interest for the incorporation of the chosen PMs into PVC-based flexible films. However, when TPE is used as the PM (curves 1, 2 and 3 in Figs. 1 and 2), the stress at 100% strain and the elastic modulus of the F₁ and F₂ samples exhibit noticeable increases with respect to the F₀ sample (Table II). Conversely, when PMs are ethylene-based terpolymers (EE), the stress-strain data of the F₁ and F₂ samples correspond to similar or improved behavior with respect to tensile properties of the F₀ sample. It should be noted that the plasticizing effect of DEHA leads to better tensile properties for the F₁ sample than for the F₂ sample.

Similar distinctions between TPE-based and EE-based blends were made in the study of hardness. With respect

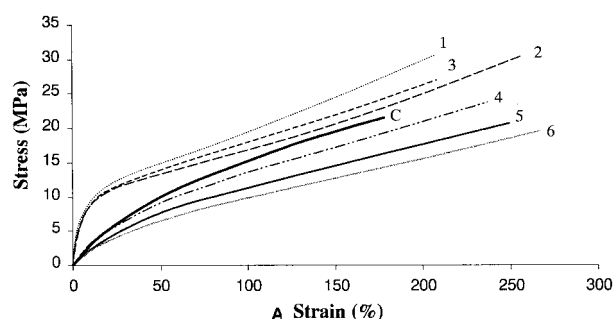


Figure 2 Stress-strain curves for F₂ samples as a function of polymeric modifier (PM): (1) PCL/TPU, (2) PE/TPU, (3) PE/TPBT, (4) EVACOh, (5) EVACO, (6) EBACO, (C) F₀ control sample.

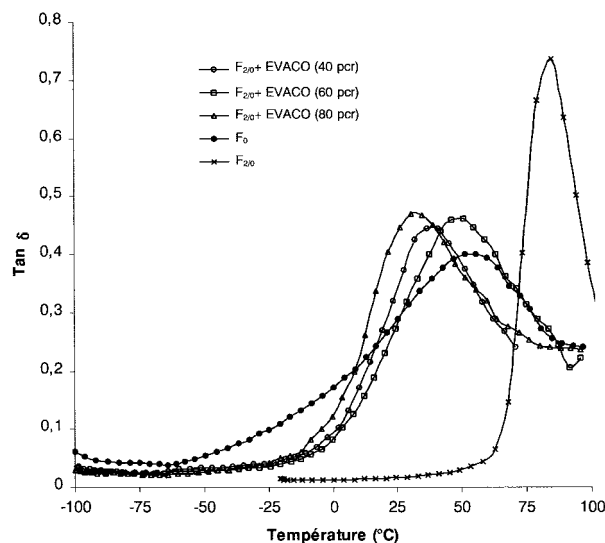


Figure 3 Mechanical loss data for plasticizer-free $F_{2/0}$ sample, for DEHA-plasticized control F_0 sample and for $F_{2/0}$ based blends with varying EVACO content.

to the F_0 sample (Shore A = 79), TPE-based blends (Shore A = 83–86) tend to be harder and EE-blends (Shore A = 78–81) tend to be of equal hardness.

Clearly, based upon the lowest T_g , the lowest elastic modulus and the lowest hardness values of the EE-based blends, EEs can be presented as the best PMs to replace DEHA for plasticizing PVC-based blends.

Plasticization and miscibility of EVACO-based blends through dynamic mechanical thermal analysis

In the EE-based blend series, the progression observed for the stress strain properties and the T_g values for EVACOh, EVACO and EBACO was in the same order as for EVACOh-based, EVACO-based and EBACO-based blends. However, incorporation of EBACO, which leads to the most satisfying properties for processing flexible films, is not appropriate for food contact, according to du Pont de Nemours technical information.²³ Therefore the softest EVACO was selected for further studies of plasticity and miscibility of EVACO-based blends.

Even if transparency is used as a criterion in polymer-polymer miscibility, it cannot be regarded as the single proof of the blend compatibility. The appearance of a single, composition dependent T_g , and of specific interactions between the two constituents of the blend is usually taken as a proof of compatibility.²²

The thermodynamic properties of EVACO-based blends obtained by adding EVACO in varying ratios (phr) to the DEHA-free $F_{2/0}$ formulation, was compared to the DEHA-plasticized standard blend F_0 . Moreover, for the best understanding of the EVACO–PVC compatibility, variation of specific polymer-poly-

mer interactions versus composition of EVACO–PVC blends was monitored by Fourier Transformed Infrared spectroscopy (FTIR).

The dissipation factor $\tan \delta$ of F_0 , $F_{2/0}$ and EVACO-based blends as functions of temperature are plotted in Figure 3. Figure 4 shows the T_g decreasing with the addition of EVACO and DEHA to $F_{2/0}$. For all blends, the existence of a single T_g illustrates the miscibility of the components. Referring to the $\tan \delta$ versus temperature curves (Fig. 3), the high peaks obtained with EVACO-plasticized blends and the broad peaks obtained with DEHA-plasticized blend, shows that the compatibility of PVC with EVACO is better than with DEHA. However, with respect to plasticization, EVACO appears to be less effective than DEHA. Indeed, as shown in Figure 4, the requisite T_g of 40°C for flexible film processing requires EVACO at 58 phr and DEHA at only 28 phr.

PVC–EVACO interactions: infrared measurements

As has been well demonstrated in polyester-based polyurethane,^{16–24} hydrogen-bonding induces a shift of the carbonyl stretchings to lower frequencies. FTIR analysis of polyester-PVC miscible blends with varying compositions have shown that molecular polymer-polymer interactions concern the carbonyl of the polyester, and this was ascribed to hydrogen bonding involving the methine proton of PVC, the α -hydrogen. This assertion was sustained by the C–D shift observed in polyester/ α -deuterated PVC blends.¹⁵ However, based upon the high miscibility of polyesters with poly(vinylene chloride)^{14–15} which does not have any α -hydrogen available, the shift of the carbonyl band was also explained by a dipole-dipole interaction between the carbonyl and the carbon-chlorine bond.¹⁴ Such dipole-dipole interaction was also supported by the miscibility of chlorinated polypropylene in which most of the α -substituents are methyl groups.²⁵ In EVACO–PVC blends, the increase in miscibility with the carbon monoxide content^{10–11,26} was explained by further interactions involving the PVC α -hydrogen and the ketonic carbonyl of CO units.²⁰

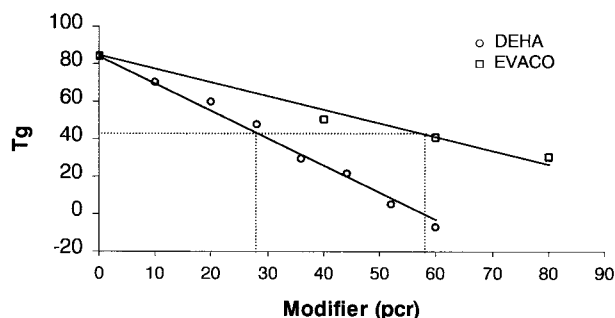
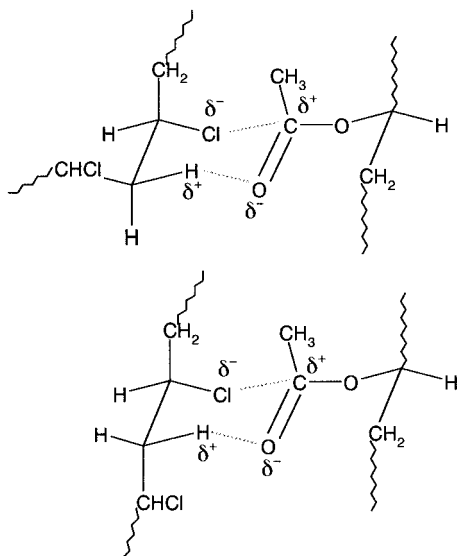


Figure 4 Plot of T_g versus modifier content in PVC-based $F_{2/0}$ blends plasticized with DEHA or EVACO.



Scheme 1 Six-center interaction between monomer unit of PVC and VA unit of EVACO.

Taking into account the calculated partial negative charge at the chlorine and positive charge at the β -hydrogen in the chloroalkanes in the syn conformation,²⁷ six center interactions (as shown in Scheme 1) could be proposed. Beside the dipole-dipole interactions, such interactions could explain the miscibility of polyester with poly(vinylene chloride) and chlorinated polypropylene.

Figure 5 shows the infrared bands of carbonyl

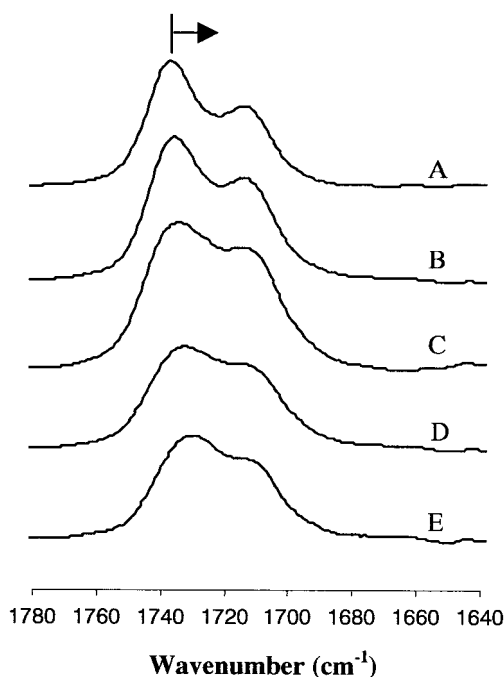


Figure 5 Variation of the C=O stretching absorption in FTIR spectra of EVACO/PVC blends: (A) 100/0, (B) 80/20, (C) 60/40, (D) 40/60 and (E) 20/80.

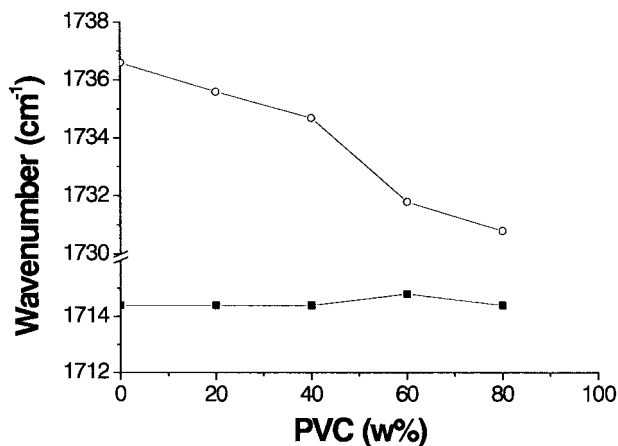


Figure 6 Wave number of carbonyl absorption versus PVC content in EVACO/PVC blends.

stretching in EVACO and EVACO/PVC blends with increasing amounts of PVC, and Figure 6 shows the variation of frequencies versus PVC content. As confirmed by the C=O stretching band of CO-free EVA copolymers²⁴ and of VA-free ethylene-*co*-(carbon monoxide) copolymers,²⁵ the bands located at 1736 and 1714 cm^{-1} in the infrared spectra of EVACO corresponds to the C=O stretching of VA and carbon monoxide units, respectively. As shown in Figures 5 and 6, only the C=O stretching band of VA units is noticeably shifted when PVC is added to EVACO. It should be noted that the six-center interaction involving a ketonic C=O in the main chain of EVACO seems sterically improbable. With respect to these observations, the improvement in miscibility brought by the incorporation of units C=O in EVA would not be the result of further interactions between the PVC and the ketonic carbonyl of EVACO but of an increase in chain flexibility, which facilitates the ester-alkyl chloride interaction.

Reduction in migration

Various analytical methods have been developed to evaluate the migration of additives from polymeric packaging into food. As it is not always possible to use foodstuffs for testing food contact materials, a large variety of food simulants accompanied by the indication of migration test conditions (times and temperatures) were described. Recently, a correlation was established between migration to isooctane at 40°C during 2 h and to olive oil during 10 days.²⁸⁻³⁰

The evaluation of the expected improvement in the migration behavior of EVACO-plasticized film was performed by comparing the migration phenomenon observed by immersion of the standard F₀ sample with those observed by immersion of EVACO-free and EVACO-plasticized samples containing decreasing percentages of DEHA. In the present work, the

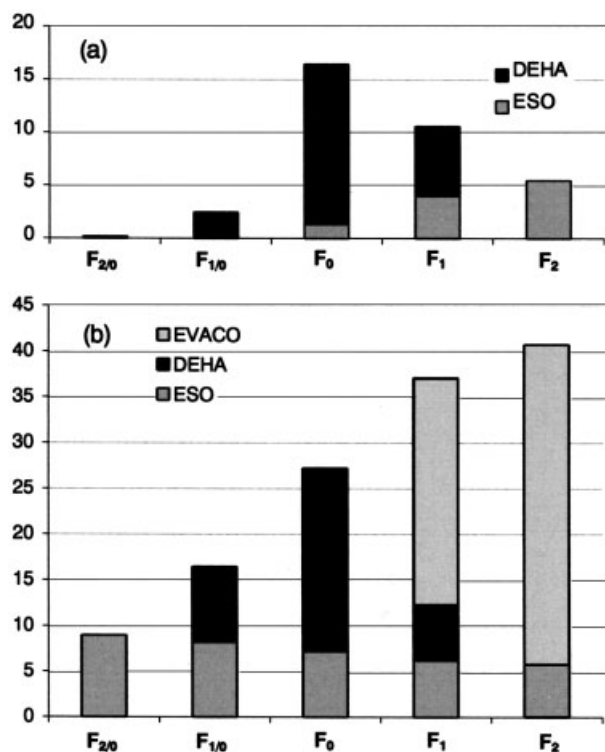


Figure 7 Correlation of (a) overall (OM) and specific (SM_D and SM_E) migrations with (b) weight percent of additives in PVC-based sample.

overall migration (OM) was expressed as the percentage of the weight loss of the sample with respect to its initial weight. Moreover, the use of isooctane has made possible the SFC identification and weight measurement of migrated DEHA and ESO. The specific migrations SM_D and SM_E were expressed as the weight percentages of DEHA and ESO respectively found in isooctane compared to the initial weight of the sample.

In Figure 7, the overall migrations (OM = SM_D + SM_E) are graphically compared to the weight percentages of the macromolecular and molecular organic compounds in the samples examined. It can be seen that the weight loss of the standard F₀ sample results from the migrations of both DEHA and ESO. OM is mostly attributed to DEHA specific migration, and the major part of DEHA initially present in the samples migrates into isooctane.

The decrease in DEHA content in the EVACO-free F_{1/0} and F_{2/0} samples causes a decrease in the overall and specific migrations. Moreover, as expected from previous studies,³¹ the decrease in the migrations is significantly higher than expected from the decrease of the DEHA content. It should be emphasized that this observation concerns both DEHA and ESO. Typically, the decrease of DEHA content from 20% in a F₀ sample to 8.2% in a F_{1/0} sample causes a decrease of OM from 16.5 to 2.5%, which is related to a concom-

itant decrease of SM_D from 15.5 to 2.3%. A simultaneous decrease of SM_E from 1.3 to 0.2% is observed for ESO contents of 7.2% in the F₀ sample to 8.2% in the F_{1/0} sample. This high decrease of the migrations as the initial content of DEHA decreases in the EVACO-free sample is explained by the concomitant loss in plasticity.

The decrease of SM_D in the EVACO-plasticized F₁ and F₂ samples also causes a decrease in the overall and specific migration of DEHA. However, in this series the decrease of the overall migration is significantly lower than expected from the decrease of the DEHA content. Moreover, the variation in the DEHA and ESO contents causes similar variations in the specific migration of ESO. Typically, the decrease of DEHA content from an initial 20% in the F₀ sample to 6.2% in the F₁ sample causes a decrease in OM from 16.5% to 10.6% and a concomitant decrease of SM_D from 15.2% to 6.5%. However, a simultaneous increase in SM_E is observed, from SM_E of 1.3% in the F₀ sample, which initially contained 7.2% ESO to SM_E of 4.1% in the F₁ sample, which initially contained 6.2% ESO. Nevertheless, it should be emphasized that, with respect to the toxicity of the migrating species, ESO is less prohibited than DEHA.

Thus, the addition of EVACO lessens the magnitude of reduction in the migration behavior obtained by decreasing the DEHA content in the standard PVC-based formulation. This attenuation is explained by the plasticizing effect of EVACO. However, the improvement is noticeable, and because of good optical, thermal and stress-strain properties, the manufacture of EVACO-plasticized PVC films without DEHA appears to be possible.

Correlation of migration behavior with plasticizing effect of additives

The migration of plasticizer from PVC-based films into solvent is generally visualized as a two-step process: (1) plasticizer diffusion in the PVC, and (2) plasticizer transfer through the PVC-solvent interface from the film to the solvent. Based on the high solubility of DEHA and ESO in isooctane, we can assume that, under the testing conditions, the diffusion is the rate-determining step for the migration. Moreover, as described for the migration of dioctylphthalate (DOP) from DOP-plasticized PVC into *n*-heptane,³² a Fickian transfer of DEHA and ESO could be expected, and the variation of the migration with the sample composition can be seen as the result of the concomitant variation in diffusivity. For the simple samples of DOP-plasticized PVC, the logarithm of diffusivity was inversely related to the initial plasticizer concentration. Such increase in diffusivity with the concentration of plasticizer was also explained by correlation of the diffusivity with the excess of T_g over test tempera-

ture.³³ It should be underlined that T_g is correlated to the plasticizer concentration and that a decrease in T_g characterizes the plasticizing effect of additives.

In a simplified analysis of the results, the weight percents of initial DEHA and ESO amounts which were transferred from PVC-based sample into isooctane at two hours were correlated to the excess of immersion temperature (40°C) over the varying T_g values of the initial sample (Table II).

Figure 8 shows a positive correlation for the transfer of DEHA. This correlation relates to the expected increase in diffusivity when the polymer is evolving from a glass to a rubber³⁴ and shows that the migration of DEHA is T_g -dependent regardless of the plasticizing system.

Figure 9 shows the correlation for the transfer of ESO. This correlation confirms that the diffusivity is lower for ESO than for DEHA and that the enhancement of migration when the polymer is evolving from a glass to a rubber is higher for ESO than for DEHA. Moreover, while the immersion temperature is above T_g for F_1 and below T_g for F_2 , the weight percent of ESO transferred is lower for F_1 than for F_2 .

These findings can be explained by the polymeric nature and the resulting lack of migration of the EVACO modifier.

For the DEHA-plasticized F_0 sample, an increase in T_g and a decrease in ESO and DEHA diffusivities occur as the migration of the plasticizing DEHA occurs. Therefore, the migration at 2 h is limited by the resulting time-dependent rate of migration. It should be noted that, for DOP-plasticized PVC, the kinetic models, taking into account the profiles of plasticizer concentration with respect to time, fit with experimental data.³²

For the polymeric EVACO-plasticized F_2 sample, because the EVACO plasticizer does not migrate, the T_g and diffusivity should not vary during the test. Therefore, the migration rate of ESO remains at its higher value over the time interval. Thus, the higher value of the resulting migration at 2 h would be the

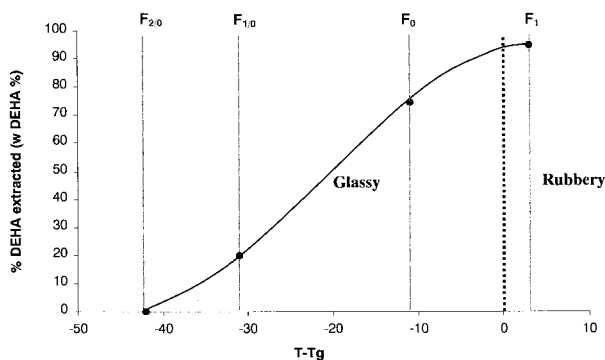


Figure 8 Weight percent of DEHA extracted versus $(T - T_g)$ with immersion temperature (T) of 40°C.

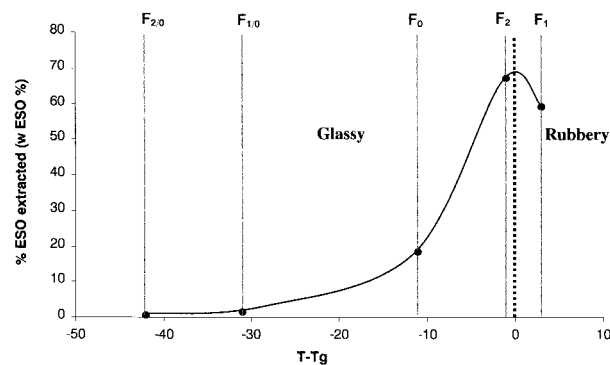


Figure 9 Weight percent of ESO extracted versus $(T - T_g)$ with immersion temperature (T) of 40°C.

result of the plasticizing effect of EVACO, the content of which makes migration occur in a stable, nearly rubbery polymer.

For the DEHA- and EVACO-plasticized F_1 sample, as DEHA migrates rapidly and EVACO does not, T_g and diffusivity should vary vastly and significantly to reach middle values in a short time. Thus, the middle value of the migration at 2 h would be due to the fast suppression of the plasticizing effect of DEHA and to the temporal stability of the EVACO content. With respect to F_2 , the lower content of EVACO makes the migration occur at a lower rate in a less rubbery polymer. It should be noted that, with respect to PVC, the solubility of DEHA and ESO with PVC/EVACO blends could be significantly different. Therefore, the combined action of solubility parameters with the rubbery parameter cannot be excluded.

CONCLUSION

While the evolution from a glass to a rubber within reasonable a temperature range can be seen as an advantage to improving processability, it appears to be a disadvantage for the prevention of additive migration. However, the incorporation of EVACO in the classical formulation instead of DEHA represents an interesting compromise in terms of the migration/processability trade-off for PVC wrap film. It makes possible a decrease of migration of the more prohibited additive, DEHA, by reducing its amount to zero. Moreover, neglecting the enhancement of the migration of ESO, which can be noted as a toxicologically less prohibited additive, the prevention of the migration of the plasticizer makes possible the temporal stability of the film properties, an improvement for customary usage.

Moreover, based on IR and thermal analysis, a six center interaction between VC and VA monomer units and the increase in flexibility brought by the CO monomer units were proposed as explanations for EVACO/PVC miscibility.

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