

Application of Fourier Transform Infrared Spectroscopy in the Study of Interactions Between PVC and Plasticizers: PVC/Plasticizer Compatibility versus Chemical Structure of Plasticizer

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Received 19 May 2005; accepted 3 October 2005

DOI 10.1002/app.23381

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Fourier transform infrared spectroscopy is applied in the study of interactions between PVC resin and plasticizers in flexible PVC systems. The comparison of the theoretical infrared spectra coming from the addition of the respective component infrared spectra with those of PVC/plasticizer experimental systems gives information about polymer/plasticizer interaction degree. In addition, solva-

tion capacity of the plasticizer varies as a function of its chemical structure, giving rise to compatibility differences between the system components. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1731–1737, 2006

Key words: polyvinylchloride; plasticizers; interactions; compatibility; FTIR spectroscopy

INTRODUCTION

Plasticized PVC is one of the most employed thermo-plastic material for everyday applications. In the majority of these applications, PVC/plasticizer mixtures are melt-processed under adequate pressure and temperature conditions. This plasticizing process takes place in two steps. In the first one, the plasticizer penetrates in PVC solid particles, making them wet. During the heating process, PVC and plasticizer melt together, giving rise to a homogeneous material.¹

However, it has been proven that under same pressure and temperature conditions, not all plasticizers have the same wetting capacity and much less the ability to make systems to melt homogeneously. This whole process, which reduces the melt viscosity with respect to the original resin, is industrially known as plasticizing. Depending on the chemical nature, plasticizers display a different interaction capacity with PVC resin. This interaction capacity between polymer and plasticizer is defined as compatibility.

A great number of studies have been devoted to develop several theories about PVC/plasticizer compatibility,^{2–6} based on different parameters that can be responsible of this compatibility, as polarity, internal pressures, dielectric constants, solubility parameters,

and modified polarity parameters. Recent publications^{7,8} have established compatibility relations as a function of plasticizer chemical nature, based on Flory original equation, modified according to the method employed in the study, specifically inverse gas chromatography^{9–12} and sol–gel transition temperature measurements.^{13–15}

In all cases, the theories are based on plasticizer solvation in PVC amorphous regions. Plasticizer/resin interactions involve electronic delocalization or bond weakness between interacting atoms or groups. Therefore, if resin/plasticizer interactions are specific of some atoms or groups, they will be affected in relation to their initial energetic state and, as a consequence, the strength of some specific covalent bonds in the polymeric matrix as well as in the plasticizer will be affected. Depending on plasticizer chemical nature, these covalent bonds will be involved in interactions at different extent and, therefore, influenced by this effect.

Accepting compatibility as a consequence of the existence of selective interactions between polymer and plasticizer, FTIR technique can be applied in the determination of the nature and strength of these interactions. This technique has been widely used in similar cases due to its sensibility to detect system spectral changes provoked by interactions¹⁶ and because it has been demonstrated to be a rapid, versatile, and reproducible technique.

However, up to now, Infrared interaction studies have been limited to spectral changes produced by strong interactions such as hydrogen bonding. Now-

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Contract grant sponsor: University of the Basque Country.

adays, however, technological advances have made possible to enlarge these studies to include less strong interactions, but quite relevant, as induced dipoles. This type of interactions are actually the ones proposed for plasticized PVC systems, basically PVC chlorine atoms and plasticizer electrophilic groups, C=O, S=O, and P=O groups.

Tiemblo et al.¹⁷ were able to determine the extension of these interactions for PVC/DOP, PVC/solvents, and PVC/PCL systems from the evolution of the carbonyl stretching vibration band peak as a function of concentration. Furthermore, these authors observed modifications in the C—Cl stretching vibration region, attributable to dipole-dipole interactions between carbonyl groups and chlorine atoms.

Induced dipole formation between these groups might induce C—Cl bond weakness in the polymeric structure and, therefore, spectral changes detectable by infrared spectroscopy. C—Cl stretching vibration bands would undergo slight shifts towards lower wavenumbers as a function of the specific plasticizer nature. This observation would permit to establish a relation between infrared spectra of several plasticized systems and plasticizer solvation capacity. This is the reason why we have selected this spectral region for being representative of all plasticized systems, independently of the chemical nature of the electrophilic groups.

In this work, we present a comparative infrared study of different PVC plasticized spectra in respect with the theoretical ones, generated by the mere addition of the component spectra without any kind of interactions between themselves. Higher spectral changes will be indicative of stronger interactions between polymer and plasticizer; in other words, a higher compatibility between both components.

In addition, we describe the effect of the chemical nature of the alcoholic part in the phthalate family as well as the effect of the acid chain length in aliphatic ester plasticizers, the substitution degree of aromatic rings in aromatic plasticizers, and finally, the effect of mixing an aliphatic ester and a phthalate type plasticizers on the relative compatibility of PVC resin and plasticizer.

EXPERIMENTAL

Materials

The PVC resin used in this work was a commercial sample named Etinox 650, supplied by Aiscondel. This resin has a *K* value of 71 and is used for the production of free flowing plasticized PVC, used for shoe soles and greenhouse applications.

Table I resumes the plasticizers employed. All phthalates were supplied by Vinilika Industrial S.L., and aliphatic esters were purchased from Aldrich.

TABLE I
Plasticizers Employed

Di-(2-ethylhexyl) phthalate (DOP)
Diisodecyl phthalate (DIDP)
Lineal phthalate C9–11 (Bisoflex 911)
Dibutyl phthalate (DBP)
Di- <i>n</i> -octyl phthalate (DnOP)
Di-(2-ethylhexyl) sebacate (DOS)
Di-(2-ethylhexyl) adipate (DOA)
Tri-(2-ethylhexyl) mellitate (TOM)
Di-(2-ethylhexylphthalate)/di(2-ethylhexyl)adipate 50/50 DOP/DOA

Characterization

DSC T_g measurements (taken in the middle point of the transition) gave a value of 83°C for PVC resin. The content of racemic diads, obtained by ¹³C-RMN analysis, was about 56%. PVC molecular weight distribution measured by GPC from THF solutions was 45,500 (M_n) and polydispersity ratio of 2.23.

Infrared spectra were collected in a Nicolet Magna 560 spectrometer at a resolution of 2 cm⁻¹ and a minimum of 32 scans were signal-averaged. Three different spectra were obtained for each sample to control reproducibility.

Plasticized PVC (30/70 w/w) samples for infrared measurements were prepared by casting from THF solutions onto KBr pellets. Films were kept at room temperature during 8 days to eliminate residual solvent. Pure PVC samples were prepared in the same way, but in this case, the films were immersed in diethyl ether to remove the solvent. Plasticizer spectra were collected from KBr pellets after plasticizer deposition on their surfaces.

RESULTS AND DISCUSSION

Infrared spectra of plasticized PVC samples

PVC infrared spectrum contains a great deal of valuable information about its molecular structure and, therefore, PVC can be considered one of the most studied polymer systems using this technique.^{18–22} Krimm et al.¹⁸ and Koenig and coworkers^{19,20} clearly defined PVC spectral characteristics long time ago, and thanks to the help of infrared technical advances, as these characteristics have been recently corroborated and extended by other investigators.^{23–25} Figure 1 shows the scale-expanded (700–600 cm⁻¹) infrared spectrum of Etinox 650 resin. This region presents basically three bands, attributable to C—Cl stretching vibrations centered at 690, 635, and 615 cm⁻¹ and whose relative intensities vary as a function of the specific characteristics of PVC samples. This group of bands is the most valuable to get information about the polymer stereoregularity.

These three bands were defined in accordance to the different order tendency of PVC chains^{1,20} as noncrys-

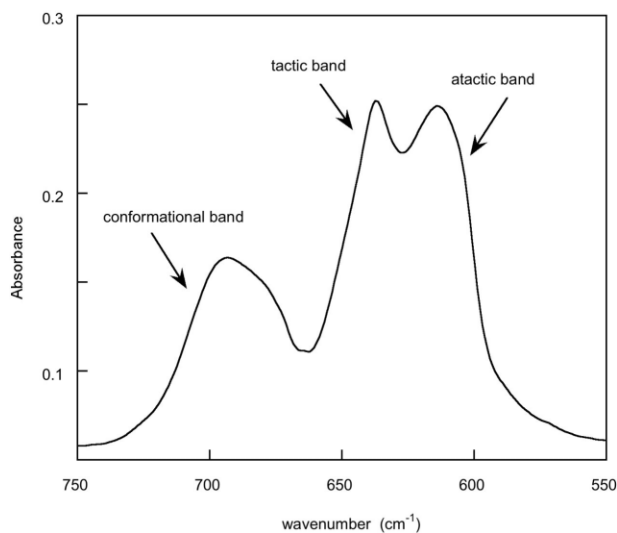


Figure 1 Scale expanded infrared spectrum of Etinox 650 PVC in the C-Cl stretching region.

talline or atactic bands (690 and 615 cm^{-1}) and crystalline or tactic band at 635 cm^{-1} . Furthermore, in PVC samples synthesized at low temperatures and using very specific catalysts, there is an additional band at 604 cm^{-1} , also defined as tactic. However, the contribution of this last band in commercial PVC resins, with only a slight tendency toward syndiotacticity, but basically considered atactic, is almost negligible versus the global contribution of the atactic band (centered at 615 cm^{-1}), in which it is overlapped.²⁰ The noncrystalline band at 690 cm^{-1} is sensitive to the less stable conformation of syndiotactic *rr* triads,¹ as well as to the more stable conformation of isotactic *mm* triads.²⁵

To facilitate the comprehension, we have divided this absorption region in three contributions or bands, namely:

- Band centered at 690 cm^{-1} : Conformational band
- Band centered at 635 cm^{-1} : Configurational tactic band
- Band centered at 615 cm^{-1} : Configurational atactic band

From an IR point of view, compatibility between two components in a mixture can be defined in terms of the presence of an interaction spectrum that differs from that of the theoretical one, resulting from the addition of the component spectra in the corresponding proportion in the mixture. Small differences in the infrared absorption wavenumbers of the interacting functional groups allow extracting information about the location of the interactions, as well as their strength. When a plasticizer, either phthalate or aliphatic ester type, is incorporated in PVC matrix, we observe in the resulting infrared spectrum small shifts of some of the absorption peak positions with respect to the theoretical ones. Basically, the plasticizer car-

bonyl stretching vibration band and C—Cl atactic band are the most interesting bands for this purpose. Although these shifts vary as a function of the plasticizer specific chemical nature, the observed effect for all the studied systems is analog.

Figure 2(a,b) shows scale-expanded infrared spectra of carbonyl and C—Cl stretching vibration regions of diverse PVC/phthalate systems, together with the resulting spectrum of the computerized addition of the spectra of both type of components. As can be seen, the carbonyl stretching vibration band of the plasticized PVC shifts from 1735 cm^{-1} (theoretical spectrum) to lower wavenumbers. In the case of the atactic C—Cl band (615 cm^{-1}), an intensity decrease together with a small shift to lower wavenumbers is observed when comparing both types of spectra. Therefore, it seems that the interaction between plasticizer and PVC resin takes place between plasticizer carbonyl groups and chlorine atoms absorbing at this specific position. These results support the idea that plasticizers interact with PVC in the amorphous or not ordered regions, as this atactic band responds to vibrations of C—Cl bonds disposed both short in syndiotactic sequences as in interchange or heterotactic sequences. These chlorine atoms have been defined by several authors^{25,26} as those having the lower activation energy, and therefore, more prone to interact.

These interactions can respond to dipole-induced dipole interactions as Tabb and Koenig proposed in the seventies.²⁰ Despite the number of studies^{27,28} about this type of interactions in similar systems, centered in the carbonyl band, we have considered more opportune to focus on the C—Cl bands as they can offer an overall vision of the type of interactions in plasticized PVC systems with any type of electrophilic groups containing plasticizer.

Aromatic plasticizers: effect of the chemical nature of the alcoholic part and the degree of ring substitution

We have chosen six different plasticizers commonly used in commercial applications. Four of them present similar chain length and molecular weight but different ramification degrees: a linear phthalate (C_{9-11}), known as Bisoflex 911; diisodecyl phthalate (DIDP); di(2-ethylhexyl phthalate) (DOP), and di-*n*-octyl phthalate (DnOP). To determine the effect of the chain length and the degree of the aromatic ring substitution, we have also included the plasticizers di-*n*-butyl phthalate and tri-*n*-octyl mellitate (TOM). We have recorded the infrared spectra of all these systems and compared with their theoretical spectra. In all cases, as a consequence of the interactions, we observe that carbonyl and C—Cl (615 cm^{-1}) bands shift to lower wavenumbers, being the shift range different depending on the system. Additionally, the band corresponding to the atactic fraction (615 cm^{-1}) flattens to a

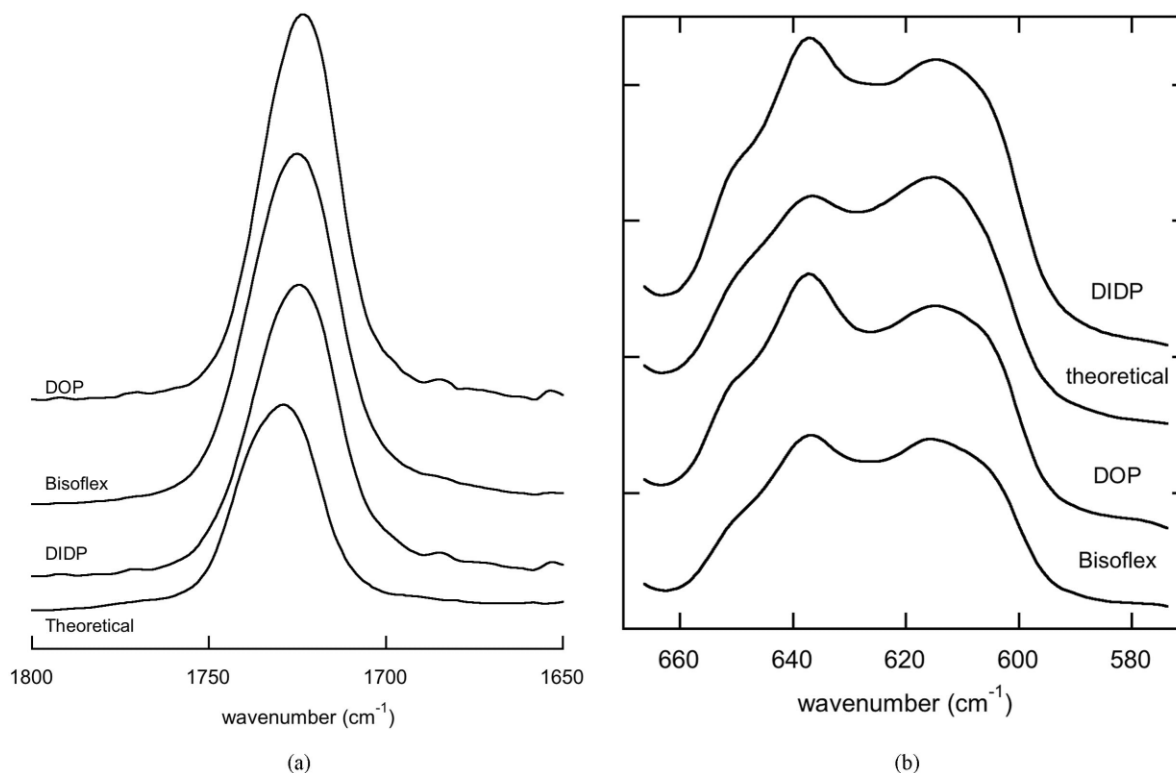


Figure 2 (a) Scale expanded infrared spectra of PVC/DOP, PVC/DIDP and PVC/Bisoflex (70/30 w/w), compared with the theoretical spectrum of PVC/DOP (70/30 w/w) in the carbonyl stretching region. (b) Scale expanded infrared spectra of PVC/DOP, PVC/DIDP and PVC/Bisoflex (70/30 w/w), compared with the theoretical spectrum of PVC/DOP (70/30 w/w) in the C-Cl configurational stretching region.

different extent depending on the chemical nature of the alcoholic part. Figure 2(a,b) shows scale-expanded carbonyl and C—Cl infrared regions for DOP, DIDP, and Bisoflex systems compared with the theoretical spectrum of PVC/DOP.

From the study of both regions, it can be appreciated that the absorption peak of carbonyl groups band for the DOP plasticized PVC suffers the biggest shift, followed by the DIDP containing system and almost null shift for Bisoflex.

The same is observed in the C—Cl stretching vibration region where the atactic band peak flattens and moves to lower wavenumbers according to the shift extent of the carbonyl group band. From these observations, it seems evident that the interaction capacity of DOP with PVC is higher than DIDP and higher than the linear phthalate, Bisoflex.

To quantify the interaction extent between plasticizers and PVC, we have calculated the atactic fractions for theoretical and experimental spectra according to eq. (1). Table II resumes the obtained results for PVC/phthalate systems.

$$f_{\text{atactic}} = \left(\frac{\text{area}_{615}}{\text{area}_{615} + \text{area}_{635}} \right) \times 100 \quad (1)$$

The interaction extent gets reflected by a decrease of the contribution of the band (615 cm^{-1}) area to the

total area of the configurational bands. With the purpose of relating all systems, we have calculated the variation percentage of the experimental fractions versus theoretical ones following eq. (2).

$$\% \text{ variation} = \left(\frac{f_{\text{atactic}}^{\text{theoretical}} - f_{\text{atactic}}^{\text{real}}}{f_{\text{atactic}}^{\text{real}}} \right) \times 100 \quad (2)$$

The results are summarized in Table III, where we have related the percentage difference value between theoretical and experimental spectra for the different studied systems. From these results, the following compatibility order can be established: Bisoflex 911 < DnOP < DIDP < DOP < DBP.

TABLE II
Infrared C—Cl Atactic Band Fractions for Different Plasticized PVC Systems (70/30 w/w), Compared with the Theoretical Values

PVC+	Atactic band fraction (%)	
	Theoretical Values	Experimental Values
DOP	58.2	49.5
DnOP	58.1	53.3
DIDP	58.2	49.8
Bisoflex	58.2	57.7
DBP	58.3	49.2
DOA/DOP	58.1	50.4

TABLE III
Percentage of Variation Between Theoretical and Experimental Atactic Band Fraction Values for PVC/Phthalate (70 : 30) Systems, Calculated According to eq. (2)

PVC	Variation (%)
DOP	17.6
DnOP	9.0
DIDP	16.8
Bisoflex	0.8
DBP	18.4

Therefore, we can conclude that the compatibility PVC/phthalate plasticizers is directly proportional to the ramification degree and inversely proportional to the alcoholic chain length.

Aromatic plasticizers: effect of the ring substitution

We have studied the infrared spectra of DOP/PVC (30/70 w/w) and TOM/PVC (30/70 w/w) to know the influence of the substitution degree of the aromatic ring on the interaction capacity of these plasticizers with PVC.

Figure 3(a,b) illustrates the position changes of the carbonyl group and C—Cl bands of PVC/TOM in comparison with their addition spectra. Comparing with the results obtained for PVC/DOP, the shifts and broadening of the bands are clearly lower for TOM plasticizer

containing system. These differences have been quantified according to eq. (2) and the results are 3.9 and 17.6% for TOM and DOP, respectively. The incorporation of a new substituent in phthalate structure decreases in an important manner the possibility of interaction between the plasticizer and the polymer, probably due to steric hindrance. Therefore, as the degree of ring substitution increases, the compatibility between polymer and plasticizer decreases considerably.

Aliphatic ester plasticizers: effect of the diacid chain length

The study compares the spectral behavior of two of the most employed aliphatic ester plasticizers in PVC formulations. We have chosen those obtained from the condensation of 2-ethyl hexyl alcohol with adipic and sebacic acids, respectively.

In this case, the observed differences in the infrared spectra, when comparing with the theoretical ones, are very similar to those already described for aromatic plasticizers: on the one side, the shift of the carbonyl stretching vibration band toward lower wavenumbers and, in the other, the broadening and shifting of the C—Cl atactic band. Figure 4(a,b) shows the spectra corresponding to these regions for the PVC/DOA system. It seems that the compatibility of these plasticizers with PVC is inversely proportional to the chain length of the diacid. These facts would be explained by a higher mobility of the adipic acid chains, leading

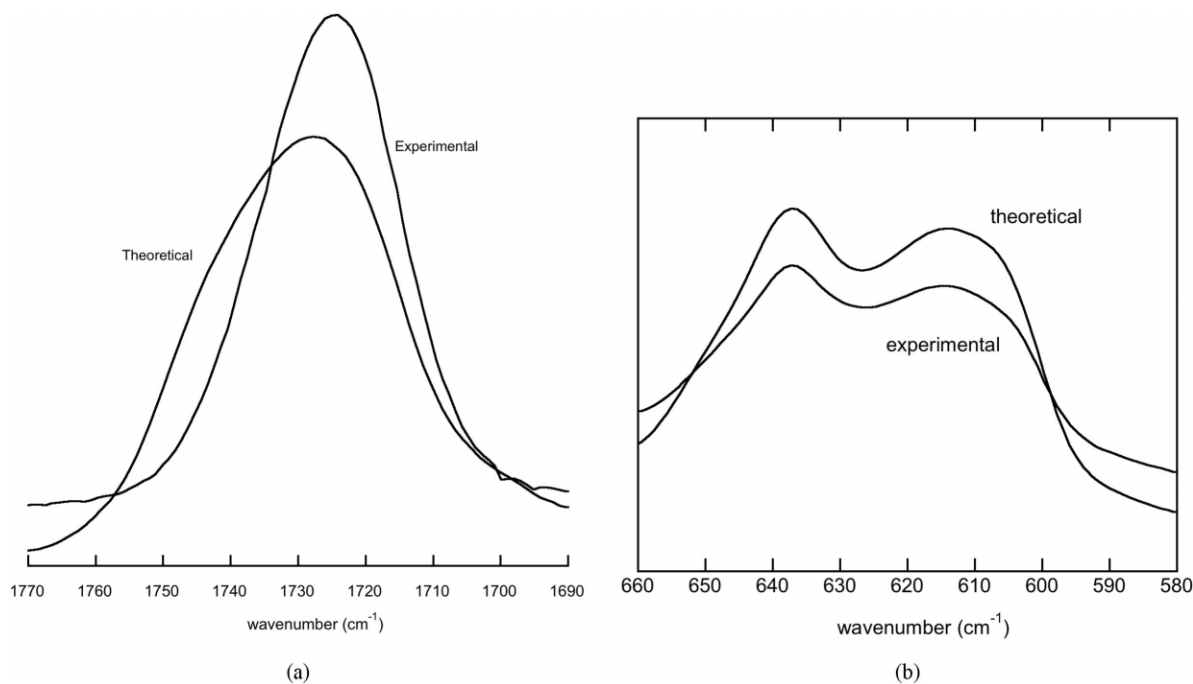
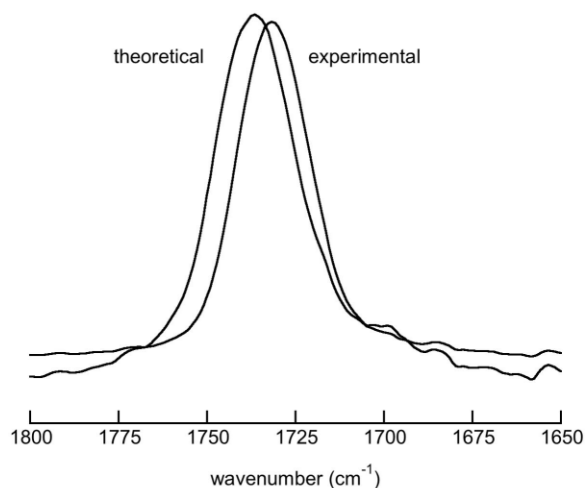
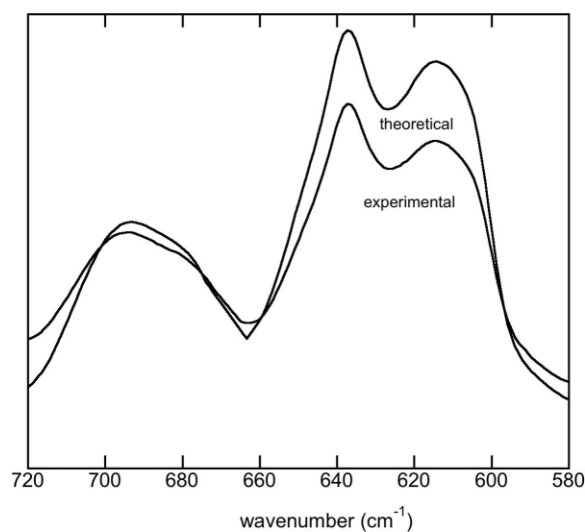


Figure 3 (a) Scale expanded infrared spectra of PVC/TOM (70/30) in the carbonyl stretching region: theoretical and experimental. (b) Scale expanded theoretical and experimental infrared spectra in the C—Cl configurational stretching region for PVC/TOM (70/30).



(a)



(b)

Figure 4 (a) Theoretical and experimental infrared spectra of PVC/DOA (70/30) in the carbonyl stretching region. (b) Theoretical and experimental infrared spectra of PVC/DOA (70/30) in the C-Cl stretching region.

to a higher interaction with chlorine atoms of PVC (13.8% for DOA versus 9.5% for DOS).

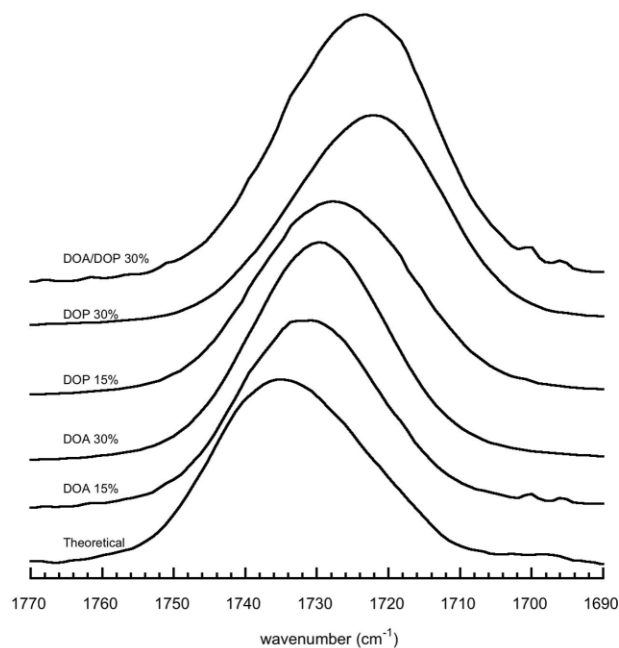
Mixture of aromatic/aliphatic plasticizers: compatibility effects with respect to pure components

Figure 5(a,b) illustrates the infrared spectra in the regions corresponding to the carbonyl and C—Cl stretching vibrations for the ternary system compared to the theoretical spectra and each of the binary systems, DOA and DOP.

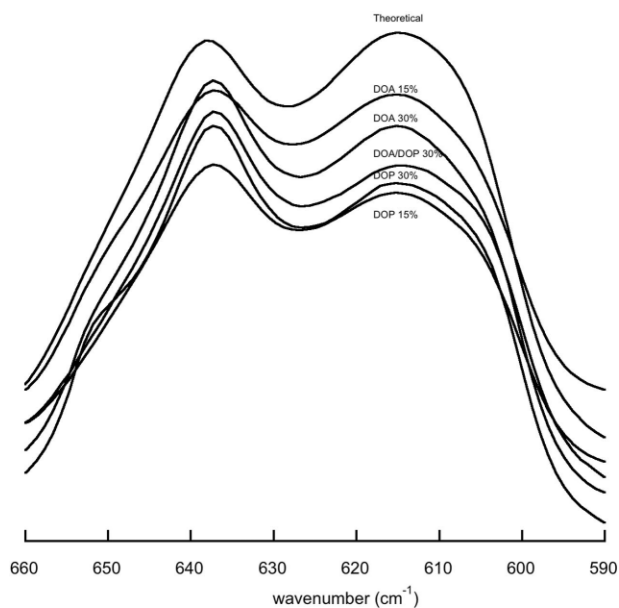
As can be seen, a shift of the carbonyl band towards lower wavenumbers is observed in all the cases. However, this shift depends on the nature of the plasticizer,

being the carbonyl band for the ternary system in between the ones of the binary systems.

Moreover, plasticization also promotes a broadening of the atactic band in relation with the theoretical spectrum. Here, again the extent of the broadening of



(a)



(b)

Figure 5 (a) Scaled expanded infrared spectra of PVC/DOA/DOP (70/15/15), PVC/DOA (70/30), (85/15) and PVC/DOP (70/30), (85/15) in the carbonyl stretching region, compared with the theoretical spectrum of PVC/DOA/DOP 70/15/15. (b) Scaled expanded infrared spectra of PVC/DOA/DOP (70/15/15), PVC/DOA (70/30), (85/15) and PVC/DOP (70/30), (85/15) in the C-Cl configurational stretching region compared with the theoretical spectrum.

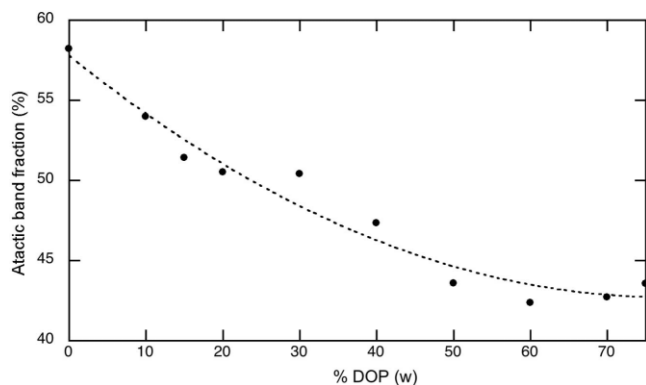


Figure 6 Evolution of the atactic band fraction of PVC versus DOP concentration.

the ternary system is intermediate between those of the binary systems. However, it is not possible to determine which one of both plasticizers participates in a higher measure to the plasticization process, as in systems where they are alone, their proportion is double with respect to the mixture.

To know the influence of each plasticizer in the interaction with PVC, we have studied the systems PVC/DOA (85/15) and PVC/DOP (85/15) and calculated the difference of the atactic band areas between theoretical and experimental spectra according to eq. (2). The reason to include these systems is based on the fact that the compatibility between PVC and plasticizer is a function of the plasticizer content, as can be observed in Figure 6, where the C—Cl atactic band fraction versus DOP concentration is illustrated.

The similarity of the results obtained for the ternary system (15.3%) and for PVC/DOP (85/15) (11.9%), compared with the value of 7.8% for PVC/DOA (85/15) is indicative that DOP has a higher interaction capacity with PVC than DOA. The higher compatibility shown by the ternary system compared with those systems plasticized with only one plasticizer at a composition 85/15, responds to the capacity of DOA to interact with PVC, although to a lesser extent than DOP.

It seems that the higher interaction capacity of DOP with respect to DOA is maintained in the ternary system, being their carbonyl groups which predominantly solvate PVC atactic part, and preventing the interaction of DOA carbonyl groups with PVC.

CONCLUSIONS

From the results obtained for all the studied systems, a compatibility order can be established, according to the chemical nature of the plasticizer as follows:

Bisoflex 911 < TOM < DnOP < DOS < DOA < DOA/DOP < DIDP < DOP < DBP

This correlation is totally in agreement with similar studies carried out by means of other methods, as those based on Flory–Huggins⁶ interaction parameters and T_g values.²⁹

Therefore, Fourier transform infrared spectroscopy can be considered as a valid technique to quantify in a relative way the compatibility between PVC and plasticizers as it is sensitive to spectral changes provoked by polymer/plasticizer interactions.

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