

Fourier Transform Infrared Spectroscopy in the Study of the Interaction Between PVC and Plasticizers: PVC/Plasticizer compatibility

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ABSTRACT: The interactions between Poly(vinyl chloride) (PVC) and Plasticizers, responsible for polymer plasticization, can be detected by means of Fourier transform infrared spectroscopy (FTIR). The interaction capacity between the two components depends on plasticizer chemical nature, PVC stereoregularity, and plasticizer content. In the case of ternary systems, consisting in PVC and two different plasticizers, their interaction with PVC depends

essentially on their chemical nature. In this work, FTIR spectroscopy is applied to determine the effect of the cited factors on the compatibility between plasticizer and resin. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1294–1300, 2008

Key words: poly(vinyl chloride); plasticizer; compatibility; FTIR spectroscopy

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the more important polymers in commercial applications. A great number of PVC based products in the market today are the applications concerning flexible PVC. Because of the PVC versatility, as it permits different and variable concentrations of a high number of plasticizers, a great diversity of PVC formulations can be found.

Plasticizers are low melting point solids or high boiling point organic liquids added to polymers to increase their workability or flexibility. Plasticization is the process through which plasticizer molecules interact with PVC polar groups, in detriment of polymer/polymer interactions. In other words, it competes with polymeric chain self-association.¹

In this way, plasticizers interact with a portion of polymer chains by its polar part, while their nonpolar section reduces the possible interaction,^{2–4} which in any case is considered a weak interaction, dipole–dipole type. The most common plasticizers are the alkyl esters of phthalic or adipic acids, which contain ester groups capable to interact with PVC and aliphatic acid chains to maintain nonpolar contact with other molecules.

About 20 years ago, Tabb and Koenig⁵ established that component interactions of a plasticized PVC based system take place between plasticizer electrophilic groups (C=O, P=O) and PVC chlorine atoms. At that time, Infrared spectroscopy already had the capacity to detect spectroscopic differences between experimental flexible PVC spectra and their corresponding additive or theoretical spectra. However, as the technique was resolution limited, they were not able to detect the existence of the proposed interactions.

Induced dipoles between polymer chlorine atoms and the electrophilic groups of plasticizer must provoke a certain weakness of polymer carbon/chlorine covalent bonds. This weakness should induce spectroscopic changes in the C–Cl stretching vibration region. Basically the C–Cl stretching vibration band should undertake a slight shift towards lower wavenumbers. Therefore, depending on plasticizer chemical nature, the shift extension would vary and these differences would allow us to obtain a relation between spectroscopic change degree and compatibility.

Many studies have been devoted to discuss different theories about the compatibility between PVC and plasticizers,^{6–9} focussing their works in the effect of several parameters as polarity, internal pressure, dielectric constants, solubility parameters, etc. In all cases, the theories are based upon the compatibility as a result of plasticizer solvation in PVC amorphous regions. Commercial PVC, synthesized at temperatures in the range of 60–80°C, is considered basically an amorphous polymer but with a certain tendency towards syndiotacticity. However, more syndiotactic

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resins can be obtained at lower processing temperatures. The lower the polymerization temperature, the higher is the syndiotactic degree,¹⁰ according to X-ray diffraction measurements.¹¹

We present in this work the results of the influence of different parameters on the compatibility between PVC/plasticizer by means of the Fourier transform infrared spectroscopy (FTIR) technique. As the interactions are proposed to be selective between the polymer amorphous regions and the plasticizer electrophilic groups,¹² compatibility must vary as a function of polymer tacticity and quantity and polarity degree of the electrophilic groups taking part in the interaction. Therefore, we have studied the effect of the nature and concentration of several plasticizers and polymer stereoregularity on the relative PVC/plasticizer compatibility.

EXPERIMENTAL

The PVC resin employed in this work is 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.

The content of racemic diads, calculated by ¹³C NMR analysis is about 56%. *T_g*, taken as the midpoint of the transition, measured by DSC is 83°C and Mn 45500 with a 2.23 polydispersity, measured by size exclusion chromatography.

Diisodecyl phthalate (DIDP) and di(2-ethylhexyl) phthalate were purchased from Vinilika Industrial S.L.

Different syndiotactic degree PVC resins were obtained in the laboratory. Samples 1, 2, and 3 were prepared by bulk polymerization at 90, 75, and 50°C, respectively, using 2, 2' azobisisobutyronitrile (AIBN) as initiator. Samples 4 and 5 were prepared by the same method using UV irradiation for decomposing AIBN at 0 and -50°C, respectively. Synthesis full details have been already published.^{13,14}

Plasticizer/PVC samples were prepared by mixing the components in THF, with the exception of the system based on PVC synthesized at -50°C, due to its partial solubility in this solvent. In this case, sample films were obtained by hot pressing at 160°C during 3 min at a pressure of 10 Tons.

Pure plasticizer infrared spectra were obtained from films coated on KBr pellets. Infrared spectra of the different PVC resins, excluding the one synthesized at -50°C, were also obtained from films cast from THF solutions onto KBr pellets. Infrared spectra were recorded on a Nicolet spectrometer, model Magna 560, using a minimum of 32 coadded scans at a resolution of 2 cm⁻¹. All the spectra shown in

this work are the average of three spectra obtained for each system.

RESULTS

Different systems of Etinox 650 with phthalate and adipate type plasticizers and their 50/50 (w/w) blends at different compositions were employed. In all cases, the incorporation of the plasticizer into the system induces spectroscopic changes with respect to the theoretical spectrum, obtained from the weighted addition of the component spectra, according to their concentration in the system. Although the extension of these changes varies from system to system, as a function of plasticizer chemical nature and its content in the mixture, the experimental spectra are characterized by peak shifts towards lower wavenumbers and broadening of the bands centred at about 1720 and 615 cm⁻¹, respectively, when compared with theoretical spectra. These positions correspond to the stretching vibrations of plasticizer carbonyl groups and C—Cl bonds, included in both short syndiotactic and heterotactic sequences. These shifts are attributable to interactions between the components of the mixture, and according to Tabb and Koenig⁵ are of induce dipole nature.

The band shift of interacting C—Cl bonds with the plasticizer provokes a decrease of its relative area with respect to the global contribution of tactic sensitive C—Cl bands (635 and 615 cm⁻¹). This area decrease can be explained upon the basis that part of its area falls out of the integration limits, established as the vibration region of C—Cl bonds disposed in syndiotactic sequences.^{5,15,16}

The higher the relative changes of the band fraction centred at 615 cm⁻¹, between theoretical and experimental spectra, the higher the interaction between polymer and plasticizer, and, therefore, more compatibility between plasticizer and resin.

We can, thus, compare the relative compatibility of the different systems from the results obtained following eq. (1), where higher change values are indicative of higher degree of compatibility between the components.

$$\% \text{ change} = \left(\frac{f_{\text{atactic}}^{\text{theoretical}} - f_{\text{atactic}}^{\text{real}}}{f_{\text{atactic}}^{\text{real}}} \right) \quad (1)$$

where the atactic fraction is defined, according to eq. (2), as the band area centred at 615 cm⁻¹, with respect to the global area of the two configurational bands, in the absorption region of C—Cl bonds.

$$f_{\text{atactic}} = \frac{\text{Area}_{615}}{\text{Area}_{615} + \text{Area}_{635}} \times 100 \quad (2)$$

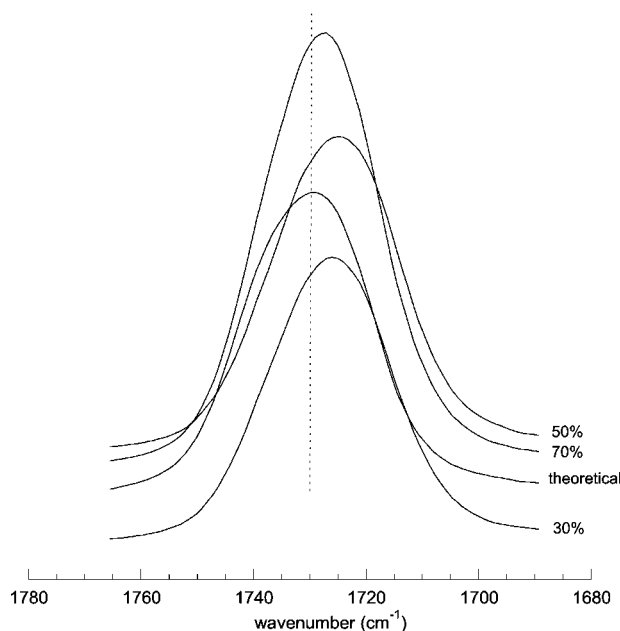


Figure 1 FTIR spectra in the carbonyl stretching vibration region for PVC/DIDP systems as a function of DIDP content (wt %), compared with the theoretical spectrum.

These values change as a function of chemical nature and concentration of the employed plasticizer.

Etinox 650/DIDP system: Effect of plasticizer concentration

Figures 1 and 2 show the infrared spectra in the stretching vibration regions of DIDP carbonyl groups and resin atactic C—Cl bonds, as a function of DIDP concentration, together with the theoretical spectra of a 70/30 (w/w) PVC/DIDP mixture. As can be seen in Figure 1, the carbonyl stretching vibration band shifts towards lower wavenumbers, if compared with the theoretical spectrum. In addition, the spectral shifts increase with plasticizer composition, up to high plasticizer contents, where the effect is less remarkable.

From the values of the f_{atactic} for both theoretical and experimental spectra (Fig. 2) and using eq. (1), we obtain a 16.8% change for PVC/DIP (70/30).

As the system components are the same in all systems, the atactic fraction values, calculated from eq. (2), are reflecting the evolution of resin/plasticizer interaction as a function of DIDP content. These values are shown in Table I. It should stress out that the higher the difference between theoretical and experimental values, the higher the interaction degree. This fact is the result of the band broadening in relation with the theoretical band. Although it is evident that the atactic fraction does not change as we are working with the same resin, the interactions between DIDP carbonyl groups and PVC chlorine

atoms, however, modify the shape of the C—Cl atactic band. Taking into consideration that the integration limits are kept constants in all calculations, a lower value implies a higher difference, and consequently a higher interaction.

Moreover, the specific interactions of chlorine atoms, disposed in short syndiotactic and/or heterotactic sequences, increase with DIDP concentration up to a value close to 60 wt %. From then on the atactic fraction starts increasing with the incorporation of more plasticizer. This is indicative of either a lower interaction possibility between PVC and DIDP or that the interactions stop being specific with certain chlorine atoms.

Thus, it seems that there is a critic point related with plasticizer content from which the incorporation of higher quantities does not produce a further increase of the specific interactions between resin and plasticizer. In this case, the critical value is about 60%.

To test the feasibility of the results, T_g of the different systems were measured by DSC. T_g values, taken in the middle point of the transition of the second scan, are summarized in Table I. T_g values

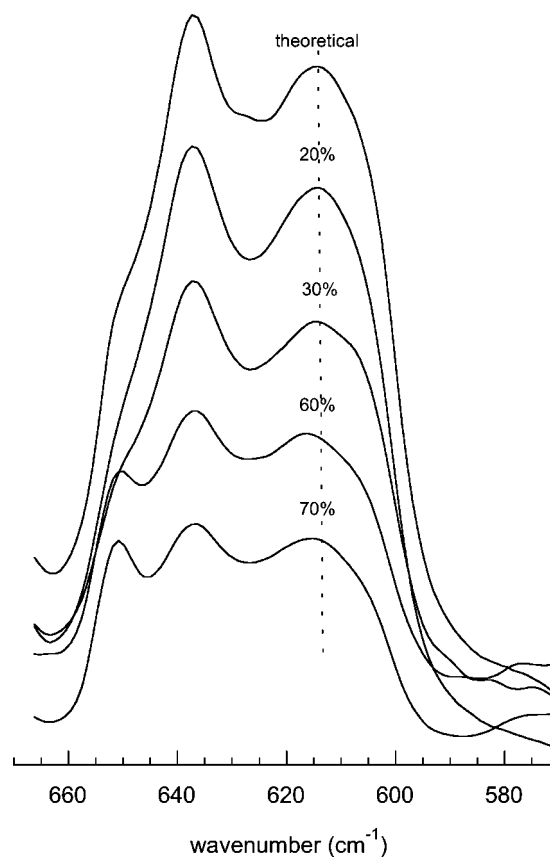


Figure 2 FTIR spectra in the C—Cl configurational stretching vibration region for PVC/DIDP systems as a function of DIDP content (wt %), compared with the theoretical spectrum.

TABLE I
Atactic Fraction (%) and T_g (°C) Values for Etinox 650/DIDP Systems

DIDP (wt %)	Atactic band fraction (%)	T_g (°C)
0	58.2	83
10	56.4	55
20	53.0	33
30	52.4	-2
40	51.8	-17
50	50.9	-43
60	47.2	-55
70	48.0	-63
75	53.3	-62

remain practically constant for those systems with a plasticizer content about 60%. This means that the action of incorporating more plasticizer does not influence this property. As plasticizer action is focussed on the improvement of processability and flexibility of the system, we can conclude that DIDP content higher than 60% is not effective.

These results corroborate those obtained by FTIR and, therefore, this technique can be considered an adequate tool to determine the plasticization critical point in flexible PVC systems.

Etinox 650/DOA system: Effect of plasticizer concentration

The above described study has been carried out for the system based on the same PVC resin and an adipate type plasticizer [di(2-ethyl hexyl adipate) (DOA)]. In this case, the value obtained from eq. (1) for the sample plasticized with DOA, 30 wt %, is 13.8%, indicative that the compatibility of this plasticizer is lower than that of DIDP at the same plasticizer concentration.

Figures 3 and 4 show the evolution of the stretching vibration bands of carbonyl and C—Cl groups as a function of DOA content. As can be seen, the results are very similar to those obtained for PVC/DIDP. The quantification of the atactic fraction evolution with plasticizer and T_g values are shown in Table II. T_g of pure plasticizer was calculated by means of Fox equation.¹⁷ For this system, plasticization critical point is between 30 and 40 wt %.

Etinox 650/DIDP/DOA system: Effect of plasticizer content

As it is a common practice to use plasticizer mixtures in commercial PVC formulations, we include in this work the study concerning a ternary system based on Etinox 650/DIDP/DOA at 50 wt % of each plasticizer.

Using eq. (1), the obtained change value for the system 70/30 polymer/plasticizer in relation to the theoretic one is 14.6%. If we compare this result with those obtained for the systems containing the same amount of DIDP and DOA (30 wt %), we could state that the compatibility of the ternary system is in between the compatibility of both binary systems. However, if we repeat the calculation, taking into consideration that the content of each plasticizer in the ternary system is 15 wt %, the change values with respect to the theoretical spectra are 11.5 and 8.0%, respectively. From these results, we can affirm that the contribution of the phthalate type plasticizer to the interaction with PVC is much higher than that of adipate plasticizer. From the infrared study of the spectral regions where interaction effects are observed (Figs. 5 and 6), we can achieve the same conclusion, that is, the ternary system behavior is closer to that of PVC/phthalate system.

In case this behavior should be fulfilled in the whole concentration range, the evolution of the polymer atactic fraction should be similar to the observed for the system Etinox 650/DIDP. Figure 7 shows the evolution of this fraction for both binary and ternary systems. In all cases, the atactic fraction of the ternary system is closer to that of the sample mono-plasticized with DIDP. This fact reflects that the interaction between polymer and plasticizer is selective towards DIDP, the more compatible plasticizer. Moreover, the plasticization critical point for the ternary system coincides with that of PVC/DIDP (60 wt %).

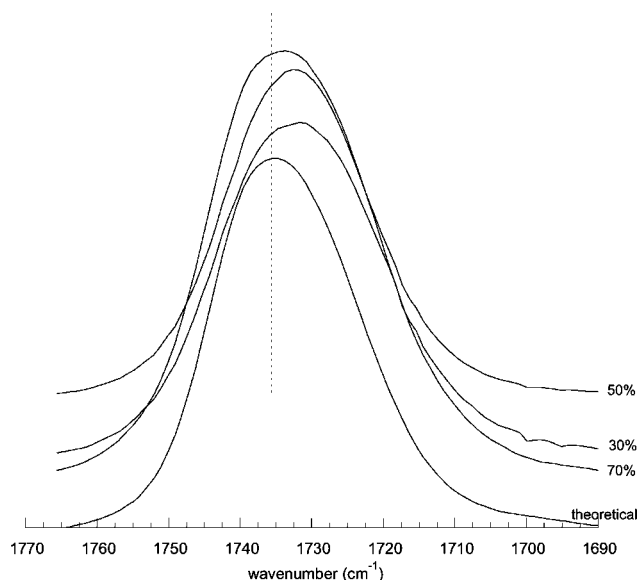


Figure 3 FTIR spectra in the carbonyl stretching vibration region for PVC/DOA systems as a function of DOA content (wt %), compared with the theoretical spectrum.

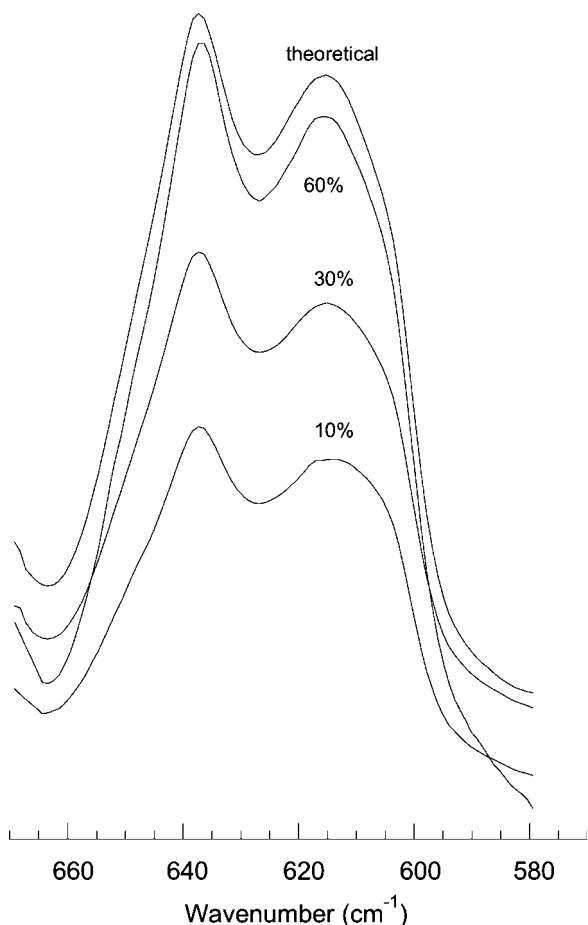


Figure 4 FTIR spectra in the C—Cl configurational stretching vibration region for PVC/DOA systems as a function of DOA content (wt %), compared with the theoretical spectrum.

Effect of resin stereoregularity on its compatibility with plasticizer

As we propose that both plasticizer electrophilic groups and PVC chlorine atoms disposed in atactic sequences are responsible of the interactions PVC/plasticizer, base resin stereoregularity is a key factor at the time of determining the interactions in flexible PVC systems.

TABLE II
Atactic Fraction (%) and T_g Values for Etinox 650/DOA Systems

DOA (wt %)	Atactic band fraction (%)	T_g (°C)
0	58.2	83
10	56.9	46
20	53.9	24
30	52.3	-16
40	52.4	-22
50	52.7	-20
60	53.4	-22
100	—	-93

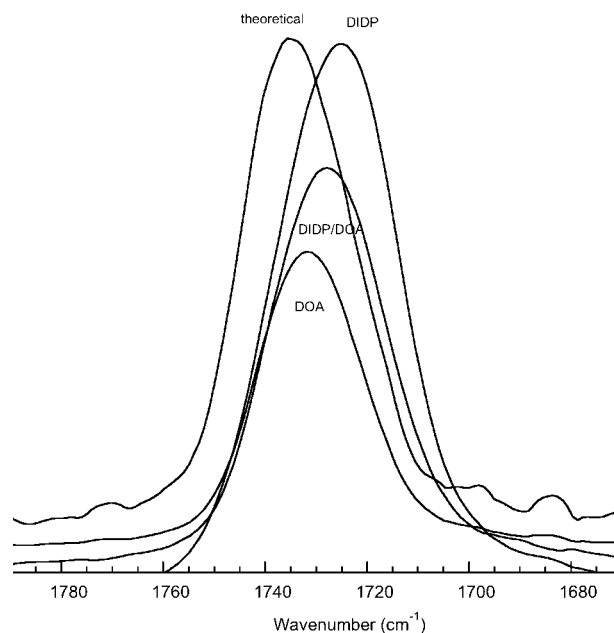


Figure 5 FTIR spectra in the carbonyl stretching vibration region for PVC/DIDP/DOA (70/15/15), PVC/DIDP (70/30) and PVC/DOA (70/30).

We have chosen DIDP as plasticizer because it presents the higher interaction capacity with PVC. Therefore, we have studied 30 wt % DIDP mixtures with resins of different syndiotacticity degree to establish a relation between polymer syndiotacticity index and its capacity to interact with the plasticizer.

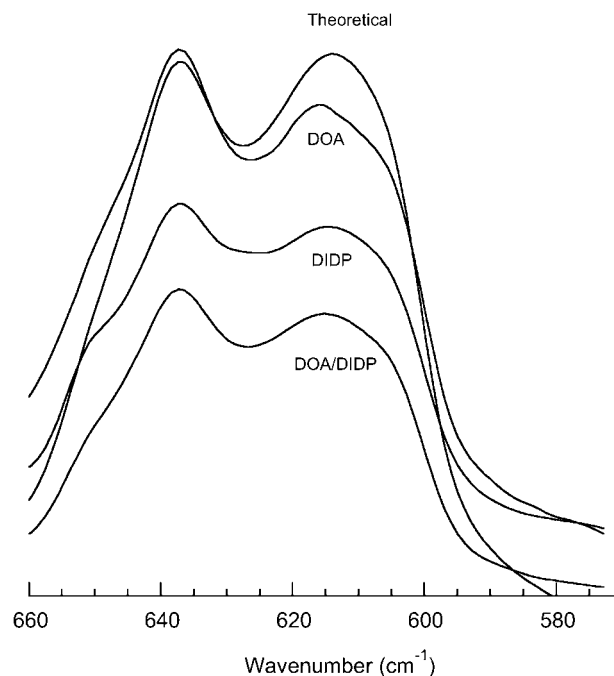


Figure 6 FTIR spectra in the C—Cl configurational stretching vibration region for PVC/DIDP, PVC/DOA, and PVC/DIDP/DOA at 30% (w/w) of plasticizer.

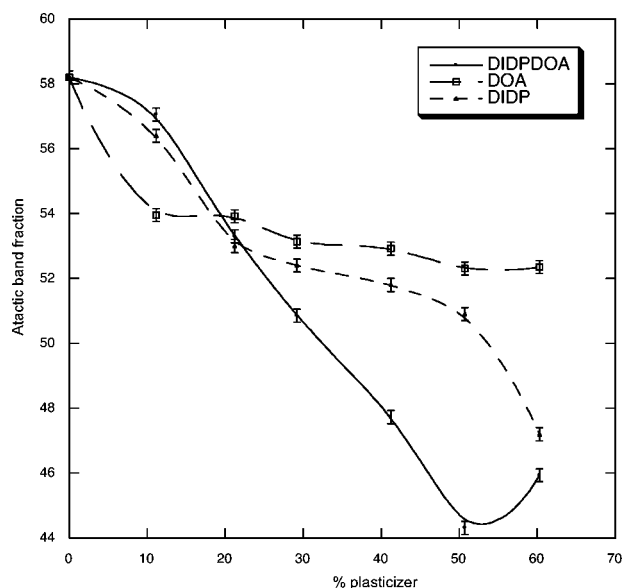


Figure 7 Evolution of PVC atactic fraction as a function of plasticizer concentration in binary and ternary systems.

Infrared spectra of three PVC resins, synthesized at different temperatures, in the C—Cl stretching vibration region are shown in Figure 8. As polymerization temperature increases the intensity of the band centred at 615 cm^{-1} increases with respect to the two configurational bands. As this band is representative of the amount of atactic disposed chlorine atoms, this is indicative of a lower resin syndiotacticity as polymerization temperature increases, as has been corroborated by ^{13}C NMR.

Table III summarizes the percentage of change, according to eq. (1), of different 30 wt % DIDP plas-

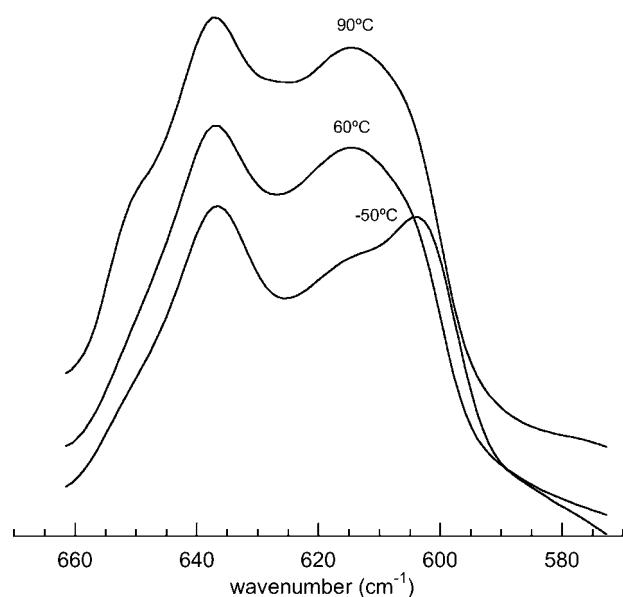


Figure 8 FTIR spectra in the C—Cl configurational stretching vibration region for PVC samples synthesized at different temperatures.

TABLE III
Percentage of Change Between Theoretical and Real Spectra for PVC/DIDP (w 30%) Versus Polymerization Temperature

Polymerization temperature ($^{\circ}\text{C}$)	Change (%)
90	4.6
75	4.2
50	1.7
0	0.6
-50	0

ticized systems as a function of polymerization temperature. In all cases, the values of each system are obtained in relation with its theoretical spectrum. From these results, we can conclude that as the polymerization temperature decreases, the difference between the theoretical and experimental spectra in the so-called atactic C—Cl band decreases. In other words, the higher the syndiotactic degree, the lower the polymer atactic fraction. Therefore, the interaction capacity with the plasticizer decreases showing a lower relative compatibility between the system components, as can be seen in Figure 9.

This fact corroborates that, effectively, polymer/plasticizer interactions take place between certain chlorine atoms, basically those in polymer chain heterotactic sequences due to their lower bond energy when compared with those syndiotactic chlorine atoms.

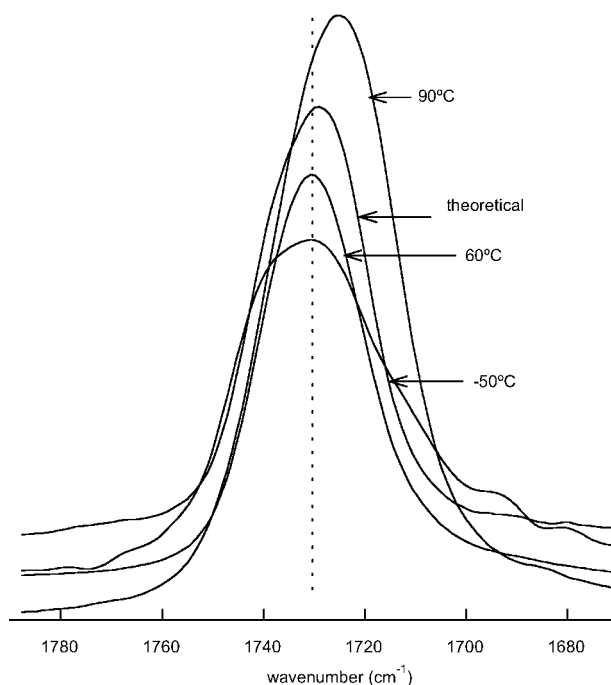


Figure 9 FTIR spectra in the carbonyl stretching vibration region for PVC/DIDP (70/30 w/w) as a function of PVC polymerization temperature.

CONCLUSIONS

The interaction between polymer and plasticizer in PVC based systems takes place between those PVC chlorine atoms, disposed in polymeric chain heterotactic sequences, and plasticizer electrophilic groups. As these interactions are selective in nature, resin syndiotacticity level, and plasticizer polarity are two fundamental variables to define the compatibility between the system components.^{2,18-20}

The higher the polarity of the employed plasticizer, the higher is its interaction capacity with the polymer. However, these interactions do not increase linearly with plasticizer concentration, as they show a critical point, from which the addition of more plasticizer does not provoke them to increase any more. This result is due to the fact that at high plasticizer concentrations, its molecules self-associate, preventing inter-association between plasticizer and polymer. In addition, this critical value increases with polymer/resin compatibility.

PVC interaction capacity with plasticizer is inversely proportional to polymeric chain syndiotactic degree, as the resultant heterotactic sequences are responsible for interaction decrease.

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