Influence of $FeCl_3$ on the Mechanical, Thermal, and Dynamic Mechanical Behavior of PVC

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ABSTRACT: PVC films impregnated with $FeCl_3$ were prepared by casting. The effect of $FeCl_3$ on the mechanical properties of PVC resembles the plasticization effect in polymeric matrices. Increasing the concentration of $FeCl_3$ results in an increase in the strain at break and a decrease in the Young modulus, in the stress at yield, and in the stress at break. A concentration of 20 wt % causes a Young modulus drop of 59% in relation to pure PVC. The plasticization effect was also confirmed by the shift of T_g to lower temperatures with an increase in $FeCl_3$ concentration. The UV/vis absorption spectrum of PVC film impregnated with 1 wt % of $FeCl_3$ shows the characteristic absorptions of the $FeCl_4^-$ ion (315 and 360 nm), suggesting the reversible formation of ion pairs responsible for the plasticization.

Introduction

Carbon black is the main additive used in the plastic industry to obtain electrically conducting polymers and composites.[1] However, it is heterogeneously distributed in polymer blends and markedly changes the mechanical properties of the polymeric matrices at concentrations lower than those necessary to reach the percolation threshold. Rao and Chopra[2] showed that the incorporation of 4 wt % of metallic salts, such as $CoCl_2$, $CuCl_2$ and $FeCl_3$, in poly(vinyl chloride) (PVC) films results in an increase in the electronic conductivity of 6 orders of magnitude. By infrared spectroscopy, the authors concluded that this effect was caused by specific interactions between the metallic ion and the C−Cl bond in the PVC chain. Other authors assigned these changes in the infrared spectra of PVC films to the presence of solvated metal salt complexes.[3] The incorporation of these salts, however, is deleterious to the polymer matrix, because metallic chlorides such as $ZnCl_2$, $SbCl_3$, and $FeCl_3$ catalyze the thermal degradation of PVC.[4] The degradation mechanism is well-known and involves the formation of conjugated double bonds as consequence of dehydrochlorination of PVC.[5] An alternative method to increase the conductivity of PVC films is irradiation with a laser beam to induce a localized dehydrochlorination, resulting in a polyacetylene pattern on the surface of the film.[6] The drawback of this method is the low stability of polyacetylene to oxidation, resulting in a rapid loss of conductivity. These results suggest that a different method should be used to change the conductivity of PVC. We are presently studying the impregnation of PVC with $FeCl_3$ to use as a precursor for obtaining blends with conductive polymers.

PVC is a rigid and relatively hard polymer depending on the syndiotacticity degree; its crystallinity varies from 7% to 20%,[7] and its glass transition temperature (T_g) varies from 75 to 105 °C.[8] These properties can be drastically altered by the introduction of plasticizers such as dioctyl phthalate, trioctyl phosphate, dioctyl sebacate, and various low-molecular-weight polymers such as poly(propylene glycol).[9] The addition of plasticizers improves flow and, therefore, processability, reducing the brittleness of the material.[10] Despite the great interest in the study of the effect of metallic chlorides on the PVC degradation mechanism, little has been reported regarding the consequences of its incorporation on the mechanical and thermal properties of this polymer. Due to our interest in using $FeCl_3$-impregnated PVC films as matrices for production of polypyrrole blends,[11] we have studied the thermal, mechanical, and dynamic mechanical behavior of PVC films with different $FeCl_3$ concentrations.

Experimental Part

Films were prepared by the casting of solutions in dry tetrahydrofuran, THF, containing PVC (Solvay do Brasil, M_n 70 000) and $FeCl_3{\cdot}6H_2O$ (Merck, 99%), at 45 °C. The concentrations of these solutions were adjusted in order to obtain 0, 1, 5, 10, 20, and 35 wt % iron salt in the polymer. The films were dried at room temperature and at temperatures above T_g under vacuum for several hours to remove residual THF and the hydration water of the $FeCl_3$.

Stress−strain tests were carried out at 25 °C on an EMIC-MEM 500 tensometer interfaced to a PC/XT microcomputer, according to ASTM D 882-64T, using a 500 N cell detector and a cross-head shift speed of 50 $mm{\cdot}min^{-1}$.

A DuPont 951 thermal analyzer was used for thermogravimetric analysis under argon flow (100 $mL{\cdot}min^{-1}$). Samples of ca. 30 mg were heated from 25 to 950 °C at a heating rate of 10 $°C{\cdot}min^{-1}$.

Differential scanning calorimetry was performed on a DuPont 910 thermal analyzer, using the following temperature program: (1) initial temperature = 140 °C; (2) cooling to −140 °C at 20 $°C{\cdot}min^{-1}$; (3) isotherm for 5 min; (4) heating from −140 to +140 °C at 20 $°C{\cdot}min^{-1}$. The DSC curves shown in this article correspond to step 4.

Dynamic-mechanical analyses (DMA) were performed on a DuPont 983 thermal analyzer. Specimens with 5 × 0.1 × 10 mm dimensions were submitted to sinusoidal deformation with 0.2 mm amplitude, at frequency of 1 Hz, in the temperature range from −100 to +150 °C and with a heating rate of 2 $°C{\cdot}min^{-1}$.

UV/visible absorption spectra for PVC films with 0.01 mm thickness impregnated with 1 wt % $FeCl_3$ and for solutions were obtained on a Beckman DU-70 spectrophotometer. FT-IR spectra for PVC films impregnated with 0, 1, and 10 wt % of $FeCl_3$ were obtained on a Perkin-Elmer 1600 FT-IR with 1 cm^{-1} resolution.

Results and Discussion

The results of stress-strain measurements for PVC films filled with 0−35 wt % $FeCl_3$ are summarized in

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Table 1. Stress–Strain Results of PVC/$FeCl_3$ Films

$FeCl_3$ (%)	Young modulus (MPa)	stress at yield (MPa)	strain at yield (%)	stress at break (MPa)	strain at break (%)	work at break ($J \times 10^{-3}$)
0	1612 ± 147	37 ± 2	3.2 ± 0.5	25 ± 4	6 ± 2	49 ± 2
1	1647 ± 63	36 ± 2	2.6 ± 0.3	33 ± 4	3 ± 1	22 ± 10
5	1603 ± 77	44 ± 3	3.1 ± 0.3	33 ± 2	5 ± 3	52 ± 14
10	1248 ± 92	31 ± 2	3.2 ± 0.3	22 ± 3	8 ± 4	98 ± 30
20	661 ± 38	16 ± 1	3.9 ± 0.2	24 ± 3	72 ± 12	540 ± 45
35	385 ± 44	7.1 ± 0.1	3.8 ± 0.6	14 ± 2	82 ± 14	388 ± 45

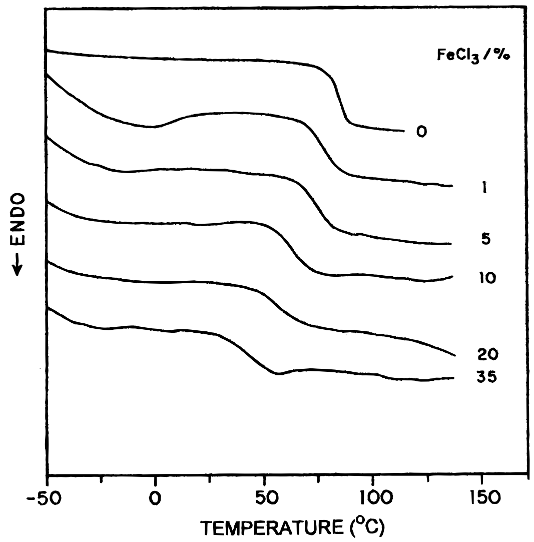


Figure 1. DSC curves of PVC as a function of $FeCl_3$ concentration. Heating rate: 20 °C min^{-1}.

Table 1. The influence of the incorporation of $FeCl_3$ on the mechanical behavior of PVC films resembles the plasticization effect. PVC is a hard and strong material[12] and shows dipole–dipole type attractions as a result of the electrostatic interactions between the chlorine atom of one chain and hydrogen of another.[13] These interactions are weakened by the presence of a plasticizer, such as dioctyl phthalate, increasing its flexibility and reducing the viscosity of the molten material, the Young modulus and the glass transition temperature.[14,15] For the PVC/$FeCl_3$ films such a conventional plasticization effect is observed, reflected by an increase in the strain at break, and by a decrease in the Young modulus, in the stress at yield and in the stress at break. This plasticization effect, which is more accentuated for concentrations above 10 wt %, produces marked changes in the mechanical properties of PVC, which vary from those of a brittle material to those of a tough material, for impregnation with 0 and 35 wt % $FeCl_3$, respectively.

In Figures 1 and 2 we can observe the influence of $FeCl_3$ concentration on the glass transition temperature (T_g) of PVC determined by DSC and DMA, respectively. The increase in ferric chloride concentration shifts the T_g to a lower temperature (see Figure 3 and Table 2), confirming the PVC plasticization effect. Besides shifting the T_g to lower temperatures, ferric chloride causes a broading of the glass transition, as can be observed from the DSC curves (Figure 1), from the peaks of loss modulus curves (Figure 2b), and from the loss factor curves (Figure 2c). The loss factor peak is broad for plasticizers classified as poor solvents for the polymer. The plasticization effect is related to weakening of the dipole–dipole interactions due to the presence of the plasticizer molecules between the PVC chains. In these PVC films impregnated with $FeCl_3$, the decrease in the dipole–dipole interactions is caused by the iron salt, which can interact with PVC chains through the formation of ion pairs, as shown in Scheme 1, that are responsible for the increase in the mobility of the chains in the glass transition region.[16–18] The ion pair can be identified by the presence of the tetrachloroferrate ion ($FeCl_4^-$), which exhibits strong absorption bands in the wavelength range from 320 to 360 nm in the UV/vis spectra and produces an intense yellow color in solution.[19] In Figure 4 the absorption spectrum of the PVC film impregnated with 1 wt % of $FeCl_3$ and the spectra of 10^{-4} M $FeCl_3$ solutions in water and chloroform are shown. The PVC/$FeCl_3$ film and the $CHCl_3$ solution show strong absorptions between 200 and 400 nm, with two characteristic bands of the tetrachloroferrate ion at 315 and 360 nm. Spectroscopic data revealed the ferric chloride can exist as $FeCl_3$ and $FeCl_4^-$ in solution.[18] The $FeCl_4^-$ ion could be formed by a disproportionation process, as represented in Scheme 2 (where S can be solvent or any other species present), which has been observed in various systems such as *N*,*N*-dimethylacetamide, acetone, acetonitrile, etc.[20–22] In our case, this ion results from the interaction between PVC and $FeCl_3$, giving origin to the ion pair represented in Scheme 1.[23] The characteristic bands for the tetrachloroferrate ions are not observed in THF solutions of $FeCl_3$, in the absence or in the presence of PVC. According to Owen and Brooks,[16] the relatively strong electronic density donor effect of the solvent competes for the Fe^{3+} ions, resulting in the extensive dissociation of Cl^- ions and in the formation of solvates. These observations suggest that in PVC/$FeCl_3$ films, obtained by casting of THF solutions, the presence of $FeCl_4^-$ is assigned to strong interactions between PVC and $FeCl_3$, with generation of an ion pair. Tetrachloroferrate ion formation was previously observed by other authors in polymeric matrices such as poly(acrylic acid) and poly(methyl methacrylate).[16,17]

From DMA results can be observed a strong dependence of the storage modulus curves (Figure 2a) on the $FeCl_3$ concentration: a high $FeCl_3$ concentration is associated with a high modulus at temperatures higher than T_g. Thermogravimetric analyses (Figure 5) show that the dehydrochlorination of PVC does not occur up to 280 °C; consequently, the increase of modulus with increasing $FeCl_3$ concentration is not associated with degradation. These results suggest a very complex mechanical behavior of PVC impregnated with $FeCl_3$.

In the literature[3,16,24–27] the catalytic effect of Lewis acids on the thermal degradation of PVC has been reported. Metallic chlorides, such as $ZnCl_2$, catalyze the degradation reaction of PVC, forming a stable complex, $H^+ZnCl_3^-$, and creating a labile alyllic chloride in the chain.[16,26] This chloride is responsible for the process of formation of conjugated double bonds. The thermal stability of PVC films containing $FeCl_3$ was studied by thermogravimetric analysis. The thermogravimetric curves obtained with pure PVC powder and with PVC/$FeCl_3$ films, under argon, are shown in Figure 5. For pure PVC powder, we can observe the first weight loss

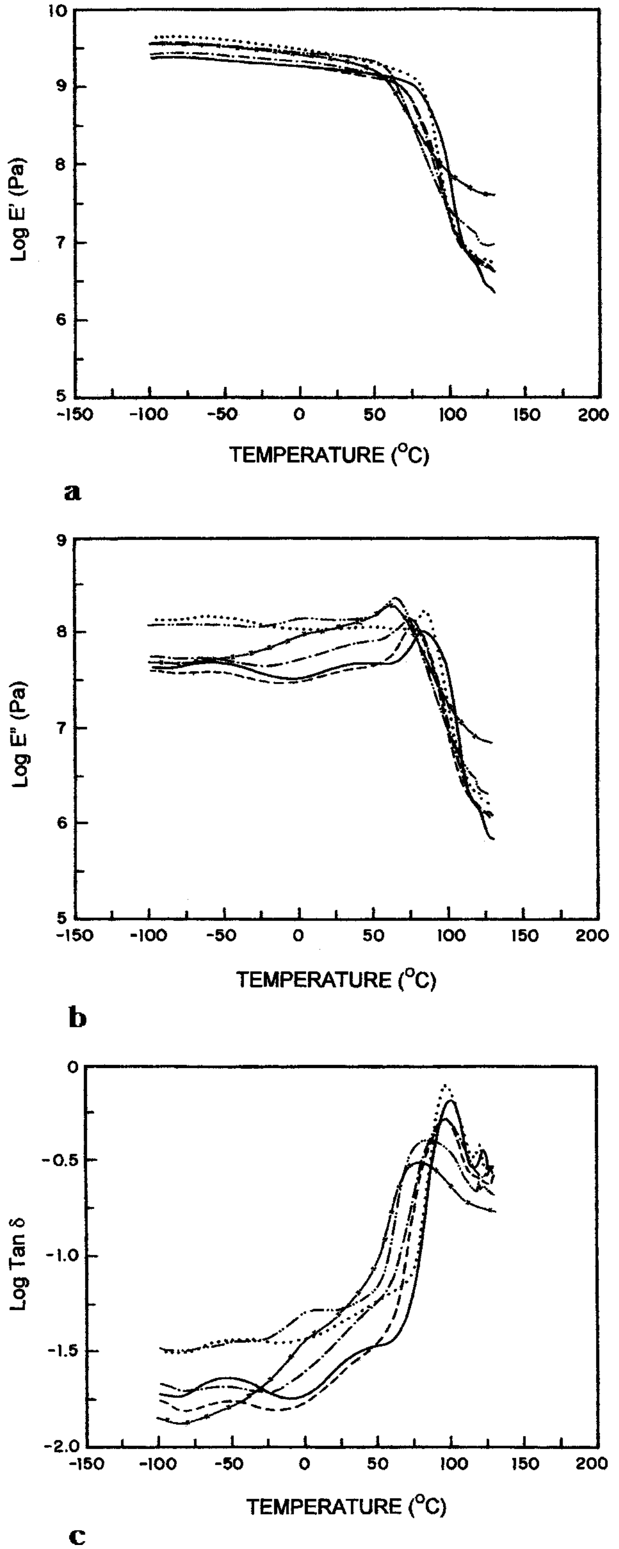


Figure 2. Dynamic mechanical behavior of PVC as a function of $FeCl_3$ concentration: (a) storage modulus ($E' \times T$), (b) loss modulus ($E'' \times T$), and (c) loss factor ($\tan \delta \times T$). Key: 0 (- - -); 1 (—); 5 (— • —); 10 (•••); 20 (— •• —) and 35 wt % of $FeCl_3$ (- × -).

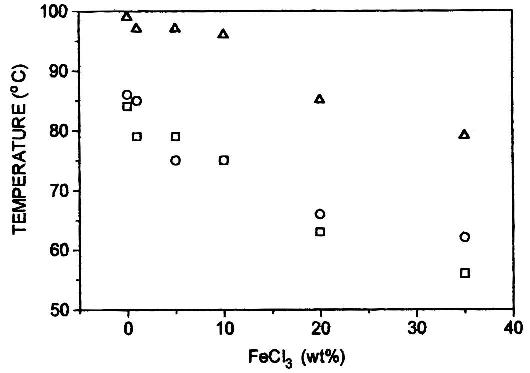


Figure 3. Glass transition temperature of PVC as a function of the weight fraction of $FeCl_3$ obtained from (○) DSC curves, (△) the maximum of the loss modulus curve, and (□) the maximum of the loss factor curves.

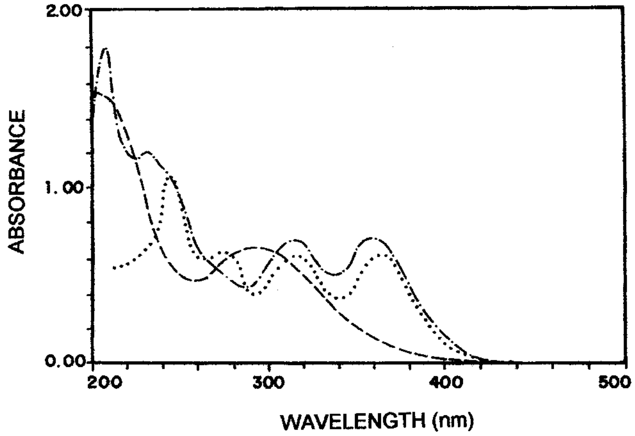


Figure 4. UV/vis absorption spectra of PVC film containing 1 wt % of $FeCl_3$ (— • —) and for 10^{-4} M $FeCl_3$ solutions in $CHCl_3$ (•••) and H_2O (- - -).

Scheme 1

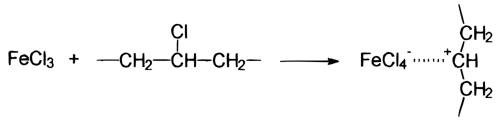


Table 2. T_g as a Function of $FeCl_3$ Concentration, Adopted as the Temperature Corresponding to the Maximum of Loss Modulus *Curves or Loss Factor Curves* and/or as the Half-Height of the Step in the DSC Curves

	T_g (°C)		
$FeCl_3$ (%)	DSC	E'' max	tan δ max
0	84	86	99
1	79	85	97
5	79	75	97
10	75	75	96
20	63	66	85
35	56	62	79

Scheme 2

$$nS + 2\,Fe^{3+}(Cl^-)_3 \rightarrow S_n[Fe^{3+}(Cl^-)_2]^+[Fe^{3+}(Cl^-)_4]^-$$

process at 280 °C, related to the dehydrochlorination reaction, occurring by a mechanism which could be either radical or ionic[28] or could be occurring simultaneously by more than one mechanism.[29] The nature of the degradation process occurring with the dehydrochlorination reaction and the catalytic effect exercised by traces of some substances such as H^+, $ZnCl_2$, and $FeCl_3$ suggest an ionic mechanism under certain conditions.[3,24] HCl catalyzes the dehydrochlorination, producing polyene sequences with lengths ranging from 6 to 14 conjugated double bonds, to a maximum of 30 units.[30] The reaction can be represented by Scheme 3. Chains, whether or not they contain conjugated double bonds, are thermally degraded to small fragments at ca. 450 °C, generating low molecular weight volatile compounds like benzene, substituted benzenes, and aliphatic hydrocarbons and causing cross-linking.[23,29]

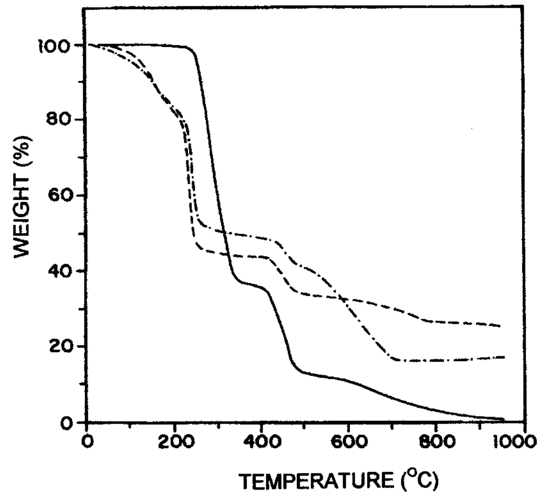


Figure 5. Thermogravimetric curves of pure PVC powder (—) and of PVC/$FeCl_3$ films as a function of $FeCl_3$ concentration: 20 (- - -) and 35 wt % (— • —). Heating rate: 10 °C min^{-1}.

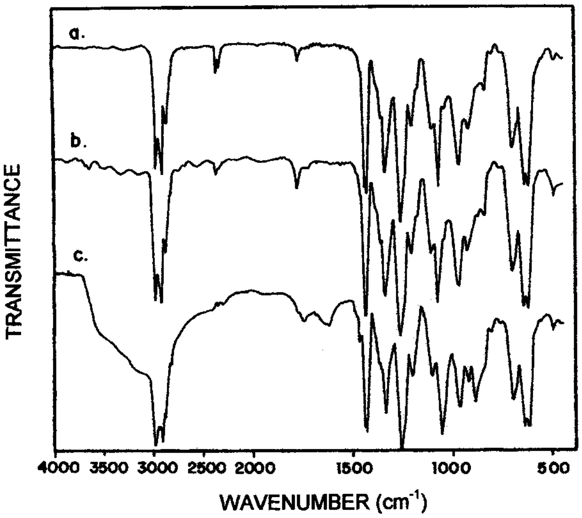
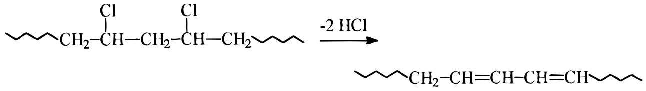


Figure 6. FT-IR spectra of PVC films as a function of $FeCl_3$ concentration (a) 0, (b) 1, and (c) 10 wt %.

Scheme 3



$$\sim CH_2-\overset{Cl}{\overset{|}{C}}H-CH_2-\overset{Cl}{\overset{|}{C}}H-CH_2\sim \xrightarrow{-2\,HCl} \sim CH_2-CH=CH-CH=CH\sim$$

Table 3. Normalized Mass Loss Obtained from the Thermogravimetric Curves of PVC Films Impregnated with $FeCl_3$ at Various Temperature Ranges

	normalized mass loss (%)				
$FeCl_3$ (wt %)	0−200 °C	200−350 °C	350−500 °C	500−950 °C	residue at 950 °C
0	0	62.6	24.6	11.7	1.1
1	0	59.0	14.6	3.7	23.6
20	0	59.3	15.1	13.9	36.8
35	0	60.6	15.7	47.7	29.8

Table 4. Glass Transition Temperature of PVC as a Function of the Weight Fraction of Carbonium Ion Segments, Determined by DSC and Predicted by the Fox Equation

		T_g (°C)	
$FeCl_3$ (wt %)	carbonium ions segments (wt %)	DSC	Fox equation
0	0	84	
1	0.2	79	83
5	1.0	79	79
10	2.0	75	74
20	4.5	63	62
35	10	56	39
100		−125[a]	

[a] Reference 33.

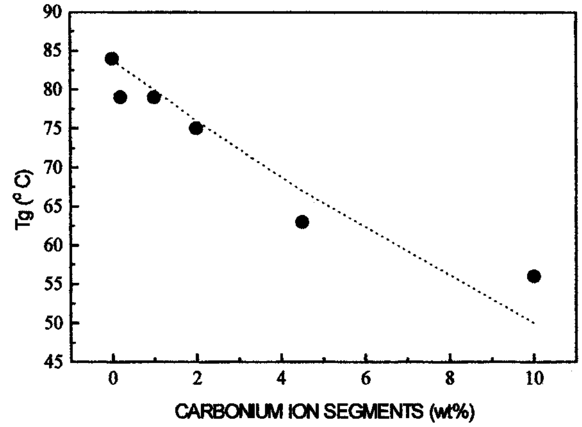


Figure 7. Glass transition temperature of PVC/$FeCl_3$ obtained from DSC experiments. The dashed curve corresponds to the predictions of the Fox equation, which describes binary plasticizers/PVC mixture.

PVC films impregnated with $FeCl_3$ are a very hygroscopic material and after prolonged exposure to the atmosphere exhibit the thermogravimetric curves shown in Figure 5, where the samples begin to lose weight at temperatures lower than 100 °C, as a consequence of the ferric chloride dehydration. In Table 3 we summarized the normalized mass loss (discarding the initial mass loss) at various temperature ranges obtained by the thermogravimetric analysis. The normalized mass loss verified in the temperature range from 200 to 300 °C is close to the expected value for pure PVC, (~58.4%), suggesting that the PVC dehydrochlorination mechanism is not affected by the presence of $FeCl_3$. Nevertheless, $FeCl_3$ appears to catalyze this process as observed by the lowering of the temperature corresponding to the maximum mass loss rate (T_{max}) with increases in $FeCl_3$ concentration: 297, 287 and 237 °C for pure PVC and PVC with 1 and 20 wt % of $FeCl_3$, respectively. T_{max} corresponds to the maximum of the derivative of weight loss curve or of the weight loss rate curve. The presence of $FeCl_3$ strongly affects the second degradation process of PVC, occurring in the temperature range from 350 to 500 °C. A lowering of weight loss in this temperature range with increasing $FeCl_3$ is observed, probably due to the network structure resulting from the dehydrochlorination reaction.

Rao and Chopra[18] and Seibles[2] studied the interactions between PVC and ferric chloride in films obtained by casting from DMF solution by IR spectroscopy. However, they disagreed with respect to the origin of the main spectral changes observed. Experiments by Maddams and Tooke[31] and Theodorou and Jasse[32] demonstrated that the interaction between conventional plasticizers, such as phthalates and phosphates, reflect on the C−Cl absorption bands occurring in the wavenumber range from 600 to 700 cm^{-1}. However, in the present work, no changes in this spectrum range were observed (see Figure 6), suggesting another plasticization mechanism for the PVC−$FeCl_3$ system. The same spectrum has no evidence of the presence of residual THF.

On the basis of these results, we suggest that the segments of PVC chains associated with the $FeCl_3$

create a heterogeneous structure with intact monomer segments and complex ionic structures, as shown in Scheme 1. The carbonium ion segments are more flexible than the monomer segment, conferring plasticization on the polymer, as observed in copolymers. On the other hand, the ionic interactions between different chains act as a physical cross-linking, resulting in a material with a strong elastic force, which cannot flow easily even at temperature ranges higher than the glass transition. The physical cross-linking should decrease the mobility of the carbonion segment, but not enough to hinder the plasticization effect. These arguments easily explain the observed behavior of the storage modulus with increases in the weight fraction of $FeCl_3$.

As a model to describe the resulting PVC structure we consider the ethylene–vinyl chloride copolymer (P(E-*co*-VC)). The carbon atoms in the ethylene segments exhibit sp^3 hybridization, while in the more flexible carbonium ion segments the hybridization of the carbon is sp^2. But the presence of a voluminous tetrachloroferrate ion restricts the free C–C rotation for carbonium ions, compensating their flexibility, so that P(E-*co*-VC) can be a good approach. The composition of the copolymer can be determined by assuming that all $FeCl_3$ molecules contribute to formation of carbonium ion segments in the PVC chain. In this case, the dependence of the T_g of PVC on $FeCl_3$ or on the carbonium ion segment concentration can be described by the Fox equation (see Table 4 and Figure 7). As the T_g of the hypothetical poly(carbonium ion), the T_g of polyethylene[33] was adopted. Glass transition temperatures of PVC/$FeCl_3$ obtained from DSC experiments are close to the values predicted by the Fox equation (except for the sample containing 35 wt % of $FeCl_3$, which shows salt segregation). The efficiency of the plasticization of PVC was determined from the slope of the line between 0 and 4.5 wt % carbonium ion segments in Figure 7: 2.8 °C/wt % carbonium ion segments of 0.44 °C/wt % $FeCl_3$. Similar results have been observed for PVC plasticized with dioctylphthalate (DOP).[34]

Conclusions

The incorporation of $FeCl_3$ in PVC matrices produces an effect similar to plasticization, as demonstrated by the shift of the glass transition temperature to lower temperatures with an increase in $FeCl_3$ concentration. The mechanical properties of PVC vary from brittle to tough with incorporation of the $FeCl_3$. There are no changes in the thermal stability of PVC upon incorporation of $FeCl_3$, as shown by thermogravimetric analysis. UV/vis spectra show the presence of the $FeCl_4^-$ ion. FTIR spectra offer evidence that the plasticization mechanism of PVC induced by $FeCl_3$ is not similar to conventional plasticizers. The plasticization effect can be related to ion pair formation between PVC and $FeCl_3$, creating more flexible segments in the chain.

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