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# Study of the Miscibility and the Thermal Degradation of PVC / PMMA Blends

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**Summary:** The aim of this paper is to study the miscibility and the thermal degradation of PVC/PMMA blends. For that purpose, blends of variable compositions from 0 to 100 wt % were prepared with and without plasticizer. Their physico-chemical characterization was carried out by differential scanning calorimetric analysis (DSC) and Fourier transform infrared spectroscopy (FTIR). Their thermal degradation under nitrogen at 185°C was studied and the HCl evolved from PVC was measured by the pH method. Degraded samples were characterized, after purification, by FTIR and UV- visible spectroscopy. The DSC analysis showed polymer miscibility up to 60 wt % of PMMA. This miscibility is due to a specific interaction of hydrogen bonding type between carbonyl groups (C=O) of PMMA and hydrogen from (CHCl) groups of PVC as evidenced by FTIR analysis. On the other hand, it was found that PMMA exerted a stabilizing effect on the thermal degradation of PVC by reducing the zip dehydrochlorination and by leading to the formation of short polyenes.

## Introduction

In recent years blending of polymers has gained significant interest. It is the cheapest way of producing materials with improved properties without laborious development of new products. This field has become economically very important.[1]

Polyvinylchloride (PVC) is one of the most important and widely used thermoplastics due to its many valuable properties like low price, good processability, chemical resistance and low flammability. Its principal drawback, however, is low thermal stability at processing temperatures. In practice, this problem is overcome by the use of stabilizers.[2] Several polymers are mixed with PVC as polymer plasticizers or processing aids. Polymethacrylates, especially polymethylmethacrylate (PMMA), are used as processing aids for PVC.[3] The first study on PVC and PMMA was done by Schurer et al.[4], who concluded that PVC was partially miscible with atactic and syndiotactic PMMA but almost completely immiscible with isotactic PMMA. The PMMA and PVC blend is a well known system in which a hydrogen- bonding type of specific

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interaction involving the α - hydrogen of PVC and the carbonyl group of PMMA is expected.[5] Polymers and their blends are often processed in the melt, which makes the thermal stability of these materials of primary importance. Several studies have shown that interactions between a polymer or its degradation products and a second polymer in the same environment, as in a blend, can alter the decomposition of the individual polymers.[6-9] I.C. Mc Neill et al.[10, 11] studied the thermal degradation of PVC and PMMA mixtures and found that the monomer formed is methyl methacrylate (MMA) from early depolymerisation of PMMA initiated by Cl radicals propagating dehydrochlorination (DHC) of PVC at a much lower temperature than that of PMMA depolymerisation when heated alone. D. Braun et al.[12, 13] studying the thermal degradation of PVC with various polymethacrylates, have shown that longer n-alkylester groups and higher concentrations of the respective polymethylacrylate exhibit some stabilization of PVC, whereas smaller ester chains and low concentrations lead to destabilization. Furthermore, they could not detect an effect of the miscibility of the samples on the thermal degradation.

In the present work, the miscibility and the thermal degradation of PVC/PMMA blends are studied. For that purpose, blends of variable compositions from 0 to 100 wt % were prepared with and without plasticizer. Their miscibility was investigated by DSC and FTIR. Their thermal degradation under nitrogen at 185 °C was studied and the HCl evolved from PVC was measured by the pH method. Degraded samples were characterized, after purification, by FTIR and UV-visible.

## Experimental

- **Materials**

Commercial grades of resins and additives listed in Table 1 were used as received. The K wert value of PVC is 67 according to the DIN 53-726 ; $\rho$ (PVC) = 0.54 g/cm$^3$; $\rho$ (PMMA) =1.18 g/cm$^3$.

Table 1. Compounds used in this study.

| Compound | Source |
|---|---|
| PVC 4000M | ENIP – Skikda ( ALGERIA) |
| PMMA | BASF ( GERMANY) |
| Lead bibasic phosphite ( heat stabilizer) | HENKEL ( GERMANY) |
| Stearic acid ( lubricant) | HENKEL ( GERMANY) |
| Di ( ethyl- 2 hexyl) phtalate (plasticizer) | BASF ( GERMANY) |

Rigid blends of PVC and PMMA of variable compositions from 0 to 100 wt % were realized. Melt mixing was performed at 185 °C on a two- roll mill, using 1 part per 100 parts PVC of lubricant and 4 parts per 100 parts PVC of stabilizer. The blends were then pressed in a hydraulic press at 185 °C for 3 min under a pressure of 150 MPa. They were water cooled under the same pressure for 2 min. The same blends of PVC and PMMA were prepared in the same conditions in the presence of 30 parts per 100 parts PVC of plasticizer (plasticized blends).

- **Glass Transitions**

The glass transitions temperatures were measured with a Perkin Elmer DSC- 7 apparatus at a heating rate of 20 °C / min.

- **Dehydrochlorination of the Blends**

The amount of liberated HCl in nitrogen (72 ml/min) was determined by using the continuous pH method at 185 ± 1°C.[14]

- **Purification of the Samples**

The samples were purified before and after dehydrochlorination by dissolution in tetrahydrofuran (THF), precipitation with distilled water and drying under vacuum at 40 °C during 72h. The purified samples were used for FTIR and UV-visible characterization.

- **FTIR Analysis**

The infrared spectra were recorded with a Philips type PU 9800 FTIR spectrophotometer at a resolution of 2 $cm^{-1}$ using KBr pellets (1 wt %). For the deconvolution of the carbonyl bands a method using the software Grams 386 was used.

- **UV-Visible Analysis**

The UV-visible spectra were recorded with a SECOMAM ANTHELIE LIGHT UV-visible spectrophotometer. Solutions of the samples were prepared in distilled THF (1g/l) and analyzed immediately.

## Results and Discussion

The glass transitions temperatures (Tg) of rigid and plasticized PVC/PMMA blends are reported in Tables 2 and 3, respectively. The glass transition is an important feature of a blend. For miscible systems, a single Tg is observed[5]. From the obtained results and according to this Tg criterion of miscibility, this polymer pair appears to be miscible up to 50 wt % PMMA. It is known that the presence of a plasticizer decreases the Tg value. In our case and for a same composition all the plasticized blends showed lower values of Tg in comparison with the rigid blends.

Table 2. Glass transition temperature of rigid PVC /PMMA blends.

| wt % of PMMA | Glass transition temperature / ° C | | |
|---|---|---|---|
| 0 | | 83.00 | |
| 10 | | 84.00 | |
| 20 | | 84.50 | |
| 30 | | 85.00 | |
| 40 | | 85.80 | |
| 50 | | 96.00 | |
| 60 | 88.70 | | 112.40 |
| 70 | 96.00 | | 113.60 |
| 80 | 100.50 | | 113.60 |
| 90 | 103.50 | | 114.50 |
| 100 | | 115.00 | |

Table 3. Glass transition temperature of plasticized PVC/PMMA blends.

| wt % of PMMA | Glass transition temperature / ° C | | |
|---|---|---|---|
| 0 | | 51.80 | |
| 10 | | 57.00 | |
| 20 | | 69.50 | |
| 30 | | 75.00 | |
| 40 | | 84.80 | |
| 50 | | 97.00 | |
| 60 | 85.50 | | 111.30 |
| 70 | 86.00 | | 112.00 |
| 80 | 98.50 | | 113.60 |
| 90 | 104.50 | | 114.50 |
| 100 | | 115.00 | |

The glass transition temperatures measured within the miscibility domain (up to 50 wt % PMMA) are reported as a function of blend composition in Figures 1 and 2 for both rigid and plasticized blends considered, respectively. A large positive deviation is observed indicating that the two polymers present a favorable specific interaction as reported by S. Shen et al.[15]

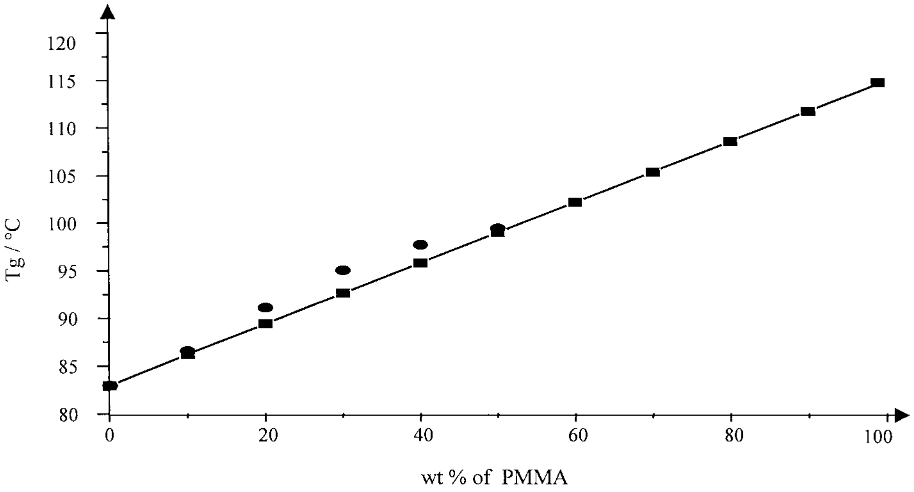

Figure 1. Glass transition temperature as a function of PMMA content in rigid PVC /PMMA blends. The line represents the behaviour based on the simple weight function $Tg = w_1Tg_1 + w_2Tg_2$, where $w_1$ and $w_2$ are weight fractions of components 1 and 2, respectively ; ■ $= Tg = w_1Tg_1 + w_2Tg_2$, ● = experimental Tg.

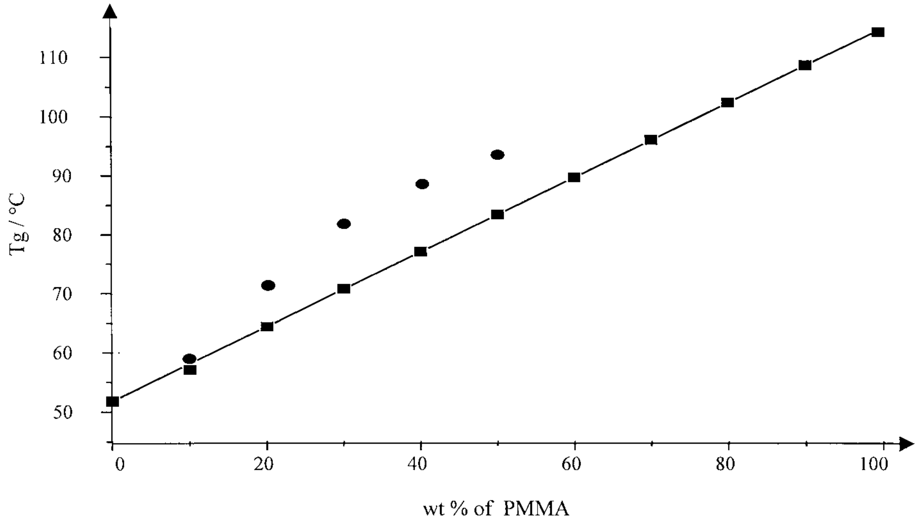

Figure 2. Glass transition temperature as a function of PMMA content in plasticized PVC /PMMA blends. The line represents the behaviour based on the simple weight function $Tg = w_1Tg_1 + w_2Tg_2$, where $w_1$ and $w_2$ are weight fractions of components 1 and 2, respectively ; ■ $= Tg = w_1Tg_1 + w_2Tg_2$, ● = experimental Tg.

FTIR analysis of the blends after purification showed a shift of the carbonyl band of PMMA to lower wavenumbers. The shift of the peak is about 3.5- 3.6 $cm^{-1}$ within the domain of miscibility of the two polymers. This feature indicates that the miscibility of PVC/PMMA blends is due to a specific interaction of hydrogen bonding type between carbonyl groups (C= O) of PMMA and hydrogen from (CHCl) groups of PVC.

In the case of carbonyl stretching bands, the high mass of the oxygen atom and the great rigidity of the bond lead to a new band which permits not only the identification of associated and non-associated groups, but also their quantification.

The deconvolution of the carbonyl band within the miscibility domain showed two contributions one corresponding to non bonded carbonyl groups in the blend (1733- 1737 $cm^{-1}$) and one at lower wavenumbers corresponding to hydrogen bonded carbonyl groups (1720-1723 $cm^{-1}$) (Figures 3 and 4).).

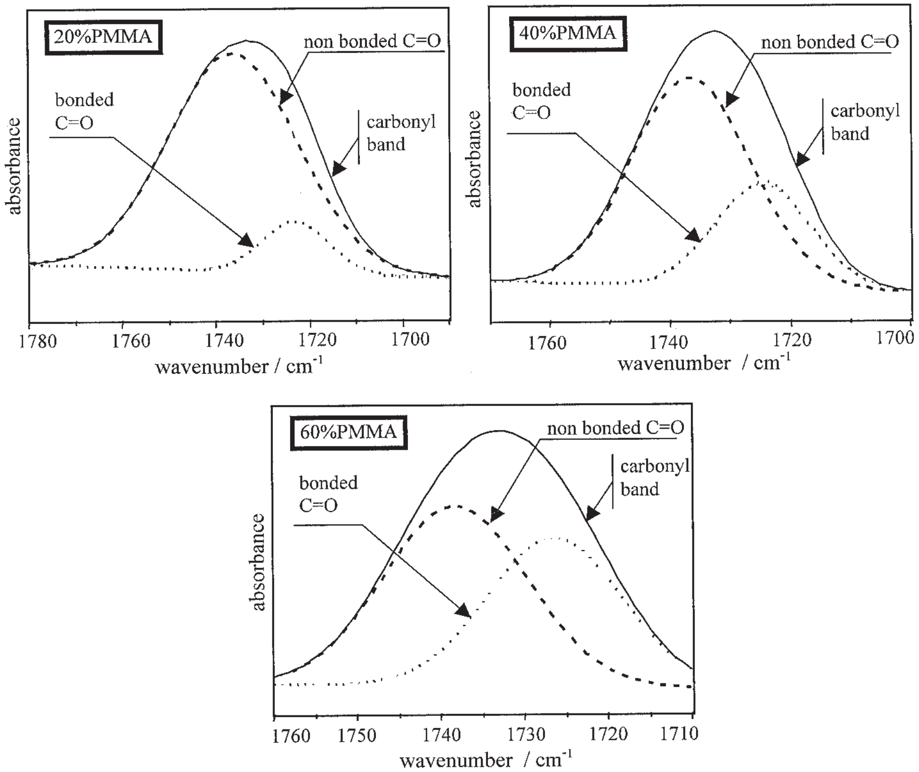

Figure 3. Deconvolution of the carbonyl band within the miscibility domain of rigid PVC/PMMA blends.

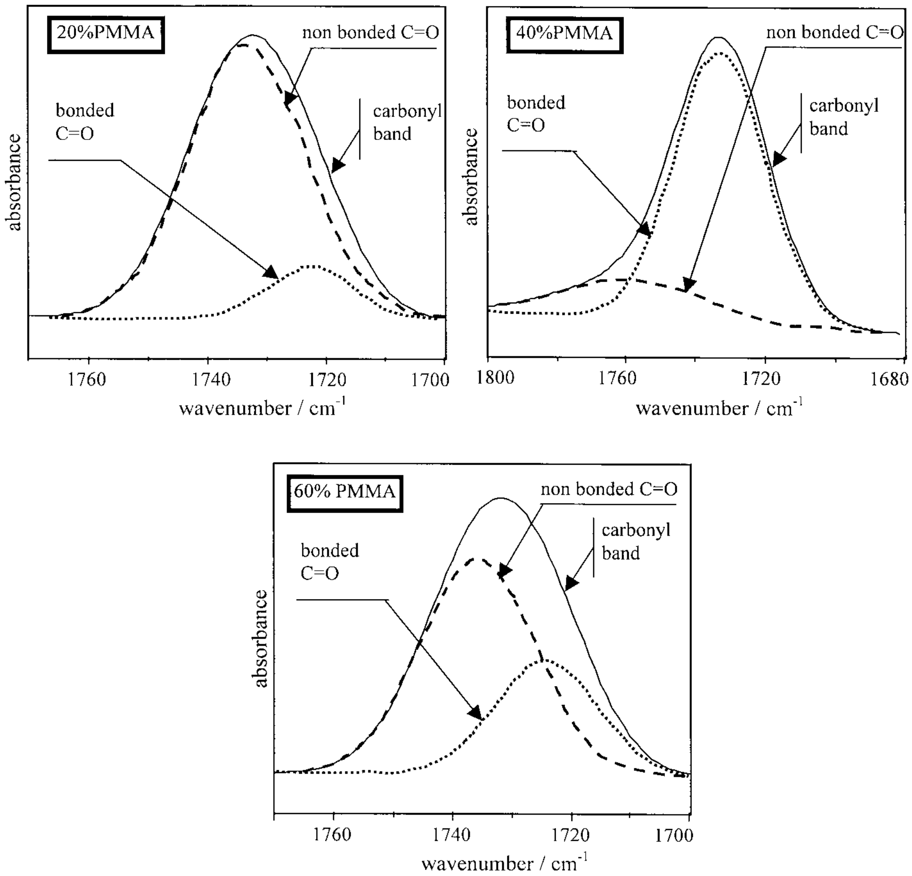

Figure 4. Deconvolution of the carbonyl band within the miscibility domain of plasticized PVC/PMMA blends.

The deconvolution of the carbonyl band outside the miscibility domain showed only contribution corresponding to non bonded carbonyl groups in the blend (Figures 5 and 6)

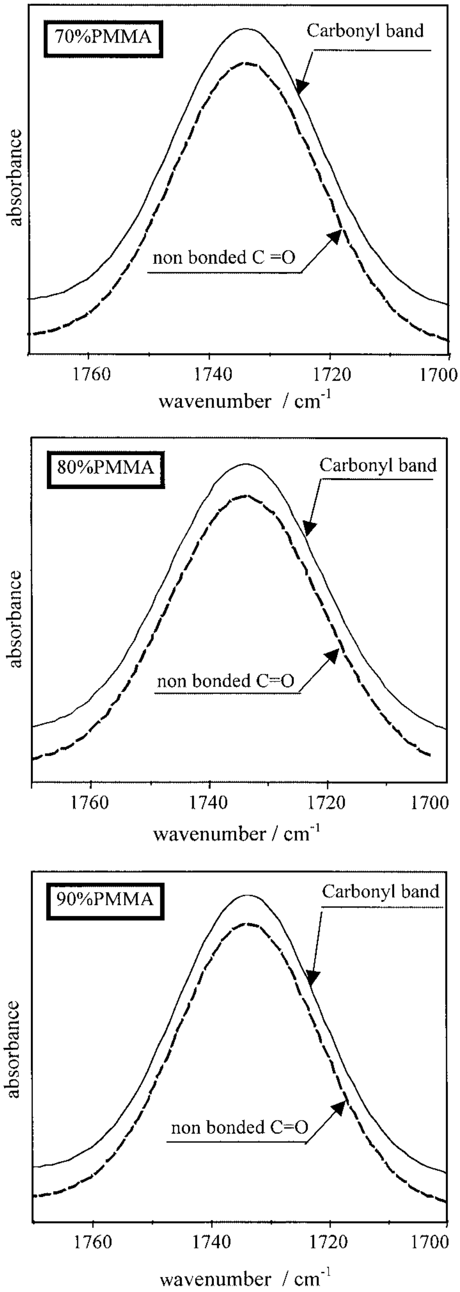

Figure 5. Déconvolution of the carbonyl band outside the miscibility domain of rigid PVC/PMMA blends.

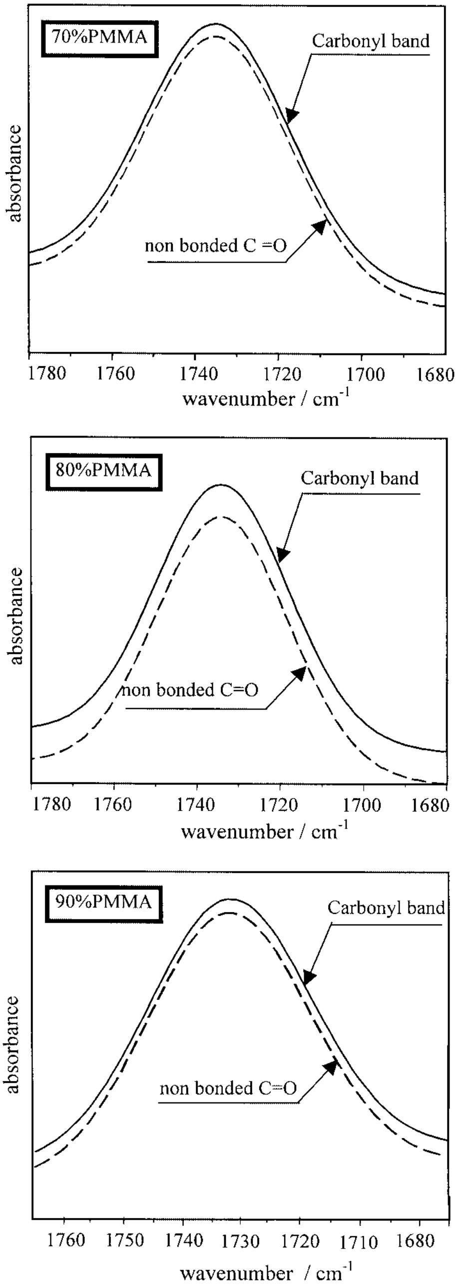

Figure 6. Déconvolution of the carbonyl band outside the miscibility domain of plasticized PVC/PMMA blends.

The thermal dehydrochlorination (DHC) of the rigid and plasticized PVC/ PMMA blends was measured at a constant temperature (185°C) in an inert atmosphere to exclude disturbing reactions of oxygen.

Figures 7 and 8 show the corresponding degradation curves.In all the blends PVC is more stable than PVC alone and the thermal stability increases with increasing the amount of PMMA in the blend.

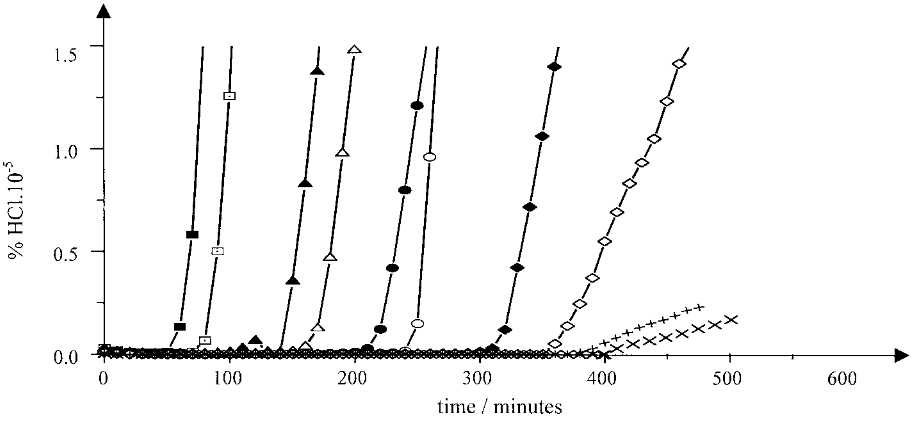

Figure 7. Dehydrochlorination curves of rigid PVC/PMMA blends at 185 °C in nitrogen; ■ = PVC, □ = 90/10, ▲ = 80/20, △ = 70/30, ○ = 60/40, ● = 50/50, ◆ = 40/60, ◇ = 30/70, + = 20/80, × = 10/90.

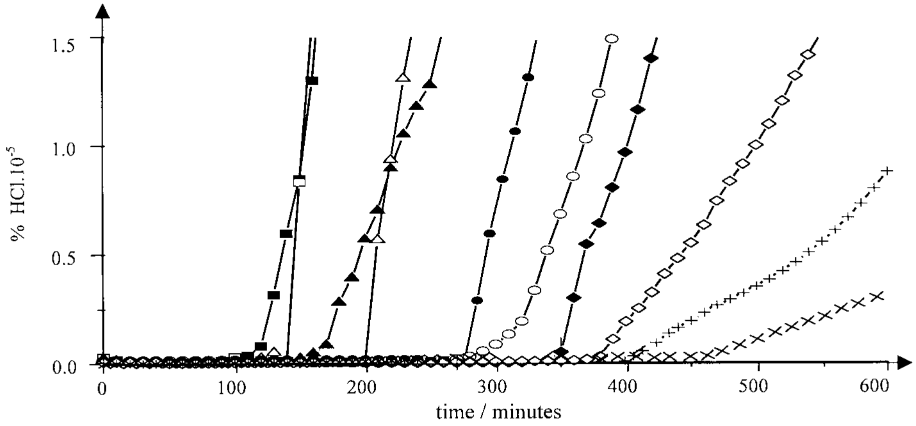

Figure 8. Dehydrochlorination curves of plasticized PVC/PMMA blends at 185 °C in nitrogen; ■ = PVC, □ = 90/10, ▲ = 80/20, △ = 70/30, ● = 60/40, ○ = 50/50, ◆ = 40/60, ◇ = 30/70, + = 20/80, × = 10/90.

Furthermore, for a same blend composition, plasticized mixtures showed longer induction times than rigid mixtures (Figure 9). The induction time is defined as the time before the accelerated DHC occurs. I. C. Mc Neill et al.[10,11] explained the best stability of PVC in presence of PMMA in terms of two processes occurring simultaneously during the degradation of the blend. The first is attack on PMMA by chlorine radicals produced during the DHC of the PVC; the second is the reaction between methacrylate ester groups and the hydrogen chloride. In our case, the presence of the heat stabilizer, which reacts with evolved HCl, gives a supplementary explanation of the observed features.

Furthermore, the linear variation of the induction time as a function of the amount of PMMA for both rigid and plasticized mixtures indicates the absence of a direct effect of miscibility on the thermal degradation of the blends.

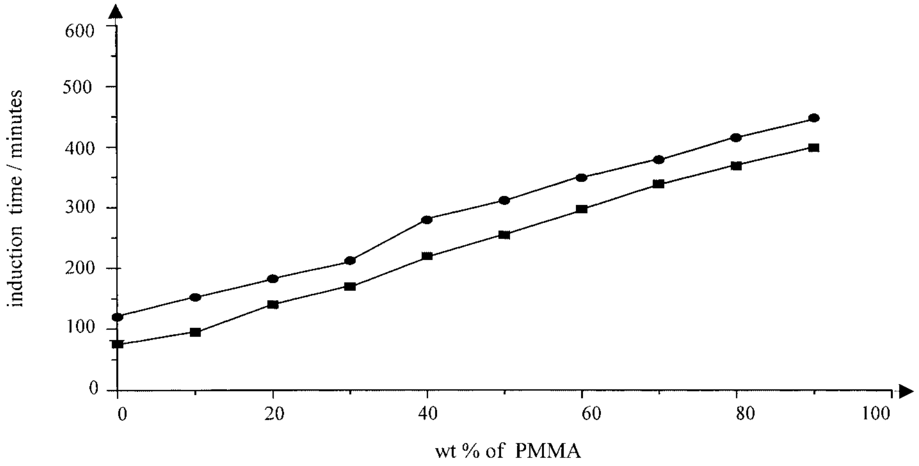

Figure 9. Variation of the induction time as a function of the amount of PMMA ; ■ = rigid blends , ● = plasticized blends.

An example of FTIR spectra of degraded samples after purification is shown in Figure 10. The appearance or disappearance of characteristic bands were not observed, but a noticeable decrease of the intensity of all the regions of the spectra was observed showing that DHC of PVC and depolymerization of PMMA have occured.

The degraded samples of PVC/PMMA blends were investigated after purification with UV-visible spectroscopy, too (Figures 11 and 12). All the spectra present the same aspect. They show clearly that the polyenes formed in the PVC in such mixtures absorb in the UV region at $\lambda < 300$ nm which corresponds to short polyenes having a number of conjugated double bonds $n \leq 4$.[16]

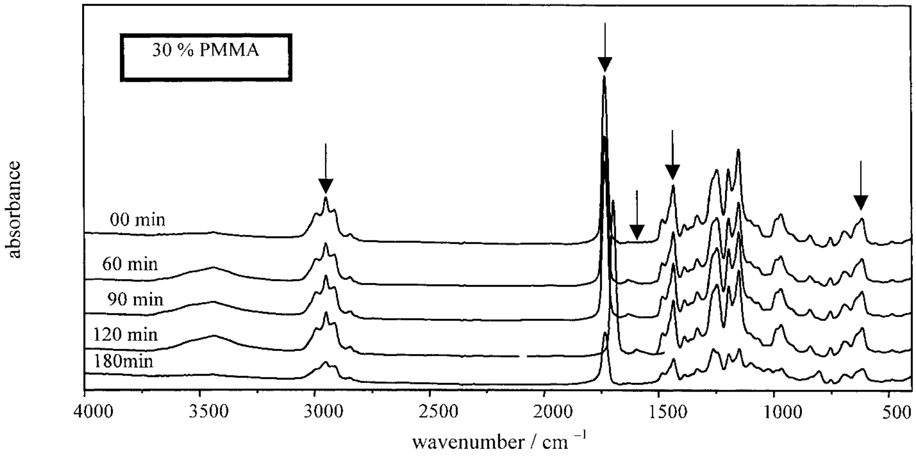

Figure 10. FTIR spectra of the plasticized blend PVC/PMMA (70/30) at various times of degradation at 185 °C.

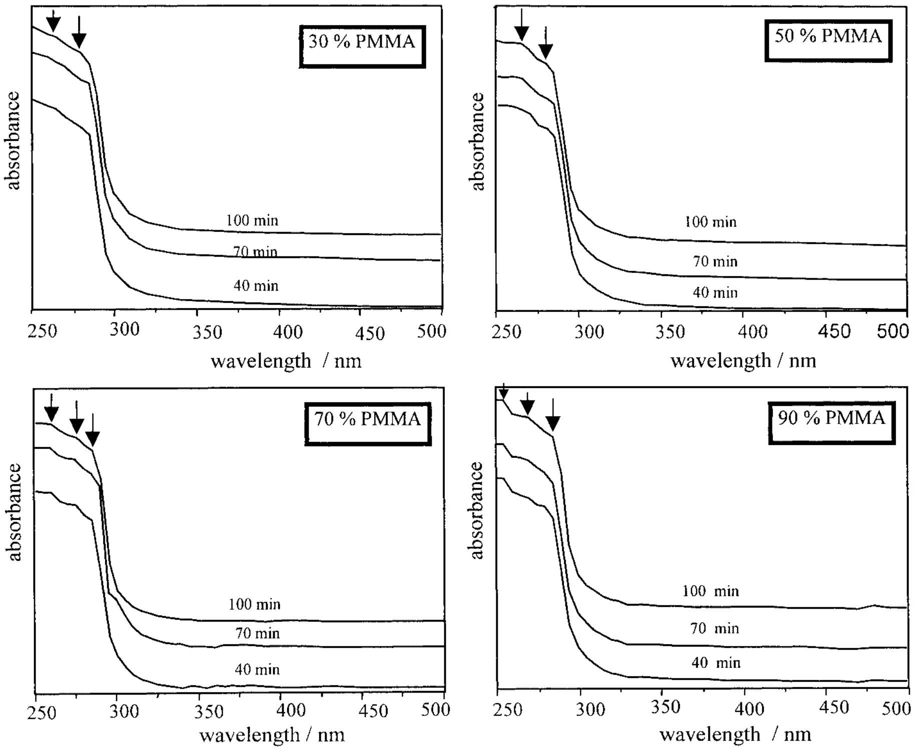

Figure 11. UV- visible spectra of rigid PVC/PMMA blends at various times of degradation at 185 °C.

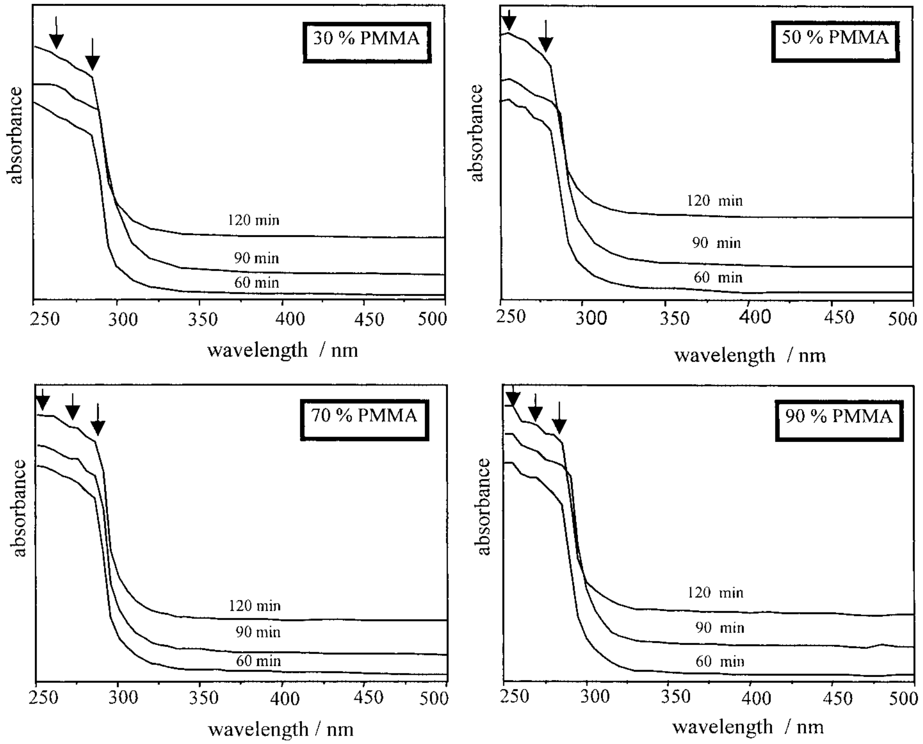

Figure 12. UV-visible spectra of plasticized PVC/PMMA blends at various times of degradation at 185 °C.

## Conclusion

The DSC analysis of the rigid and plasticized PVC/PMMA blends showed polymer miscibility up to 50 wt % of PMMA. This miscibility is due to a specific interaction of hydrogen bonding type between carbonyl groups (C= O) of PMMA and hydrogen from (CHCl) groups of PVC as evidenced by FTIR analysis.

On the other hand the results showed that PMMA exerted a stabilizing effect on the thermal degradation of PVC by reducing the zip dehydrochlorination and by leading to the formation of short polyenes. No influence of the miscibility of the two polymers was detected on their thermal degradation.

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