Study of the Properties of Rigid and Plasticized PVC/PMMA Blends

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Summary: The aim of this work is to study the structure-properties relationship of rigid and plasticized PVC/PMMA blends. For that purpose, blends of variable compositions were prepared in the absence and in the presence of a plasticizer di (ethyl-2 hexyl) phtalate or DEHP. The miscibility of the two polymers was investigated by differential scanning calorimetric analysis (DSC) and Fourier transform infrared spectroscopy. The weight loss from 30 to 600 °C was investigated by thermogravimetric analysis (TGA). The thermal degradation under nitrogen at 185 °C was studied and the amount of HCl released from PVC was measured by the pH method. Furthermore, the variation of mechanical properties such as tensile behavior, hardness and impact resistance was investigated for all blend compositions.

Keywords: DEHP; DSC; PVC/PMMA; structure-property relations; TGA

Introduction

Poly(vinylchloride) (PVC) is one of the most important and widely used thermoplastics. Its principal drawback, however, is low thermal stability at processing temperatures. Several workers[1-6] have reported on the degradation and stabilization of PVC. Several polymers are mixed with PVC as polymer plasticizers or processing aids. Polymethacrylates, specially polymethylmethacrylate (PMMA), are used as processing aids for PVC. The first study on PVC and PMMA blends was done by Shurer et al.,[7] who concluded that PVC was partially miscible with atactic and syndiotactic PMMA but almost completely immiscible with isotactic PMMA. The 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.[8,9] Polymers and their blends are often processed in the melt, which makes the thermal stability of these materials of primary importance. Mc Neill et al.[10,11] have found that the PVC is slightly less stable and

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gives monomer at temperatures corresponding to PVC dehydrochlorination (DHC). 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. More recently, Braun et al.[5] synthetized copolymers based on methacrylates and investigated them as costabilisers for PVC. They found that these polymers are capable of improving the induction time of PVC dehydrochlorination.

In a previous work,[9] we have 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.

In this paper, further investigations are done on the miscibility, the thermal degradation and the mechanical properties such as tensile behavior, hardness and impact resistance of rigid and plasticized PVC/PMMA blends.

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; ρ(PVC) = 0.54 g/cm^3; ρ(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)

Polymer Blends

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.

Thermogravimetric and Differential Thermogravimetric Analysis

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded in a static nitrogen atmosphere from 30 to 600 °C at a heating rate of 10 °C/ min using a Perkin-Elmer DSC-7 apparatus.

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 according to the ISO 182-2 (1990).

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 72 h. The purified samples were used for FTIR analysis.

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.

Mechanical Characterization

Measurements of tensile properties were undertaken using an ADAMEL LHOMARGY DY 29 testing machine according to the ISO 37 (1994).

A shore D type durometer was used for the determination of the hardness of the blends according to the NFT 51-109 (1981). The Charpy impact resistance's were determined using a WOLPERT pendulum according to the NFT 51-035 (1976).

Results and Discussion

The glass transitions temperatures (Tg) of rigid and plasticized PVC/PMMA blends are reported in Table 2. The glass transition is an important feature of a blend. For miscible systems a single Tg is observed. From the obtained results and according to the 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. Table 2 shows that for a same composition all the plasticized blends have lower values of Tg in comparison with the rigid ones.

Table 2. Glass transition temperatures (Tg) of rigid and plasticized PVC/PMMA blends.

wt % of PMMA	Tg of rigid blends (°C)		Tg of plasticized blends (°C)	
0	83.00		51.80	
10	84.00		57.00	
20	84.50		69.50	
30	85.00		75.00	
40	85.80		84.80	
50	96.00		97.00	
60	88.70	112.40	85.50	111.30
70	96.00	113.00	86.00	112.00
80	100.50	113.60	98.50	113.80
90	103.50	114.50	104.50	114.50
100	115.00			

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 carbony 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}) (Figs. 1 and 2).

The deconvolution of the carbonyl band outside the miscibility domain showed only contribution corresponding to non bonded carbonyl groups in the blend (Figs. 3 and 4).

Thermogravimetric analysis (TGA) was used to study the thermal decomposition of the rigid and plasticized PVC/PMMA blends from 30 to 600 °C. The thermal degradation of PVC in a broad range of temperatures (up to and above 727 °C) is a two-step process. The first step (up to 350 °C) mainly involves dehydrochlorination of the polymer and formation of macro-molecules with conjugated double bonds that suffer cracking during the second step (up to 550 °C).[14-16] In the first step HCl is the main volatile product (96 to 99,5 %), the amount of other products being very low including quantities of benzene and some other hydrocarbons (1 to 3 %).[14,15] In the second step the degradation of the polymer which has already become the dehydrochlorinated product continues with cracking and pyrolysis to low hydrocarbons of linear or cyclic structure (more than 170 products C_1-C_7 have been identified).[14]

Concerning PMMA, it is generally assumed that its thermal decomposition at temperatures higher than 300 °C gives statistical chains scissions followed by depolymerisation and liberation of the pure monomer.[17]

Data obtained from the thermogravimetric curves of Fig. 5 and 6 are given in Tables 3 and 4. They show clearly that for the two types of blends considered the weight losses (%) corresponding to the first step of the thermal decomposition are lower than those of PVC and PMMA. Hence it seems that PMMA exert a stabilising effect on the thermal degradation of PVC by reducing the dehydrochlorination. On the other hand, the weight losses corresponding to the second step of the thermal decomposition are higher than those of PVC. It seems that chains scissions, cracking of double bonds and depolymerisation of PMMA are more important during this second step. However, the first process is the most interesting because temperatures used in industrial processing never exceed 230 °C.

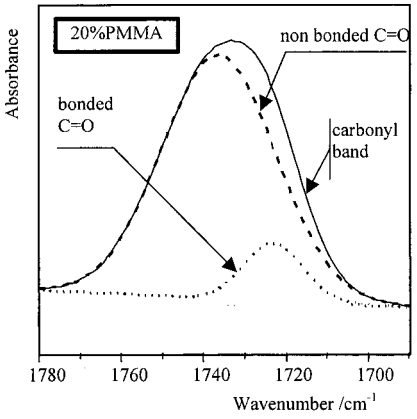

Fig. 1: Deconvolution of the carbonyl band within the miscibility domain of rigid PVC/PMMA blends.

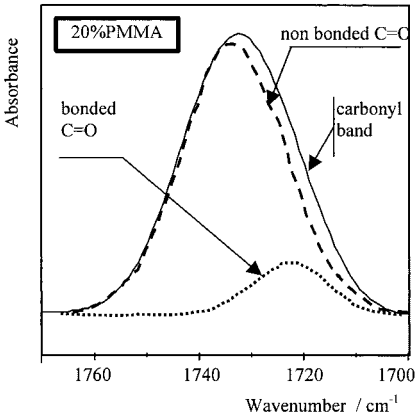

Fig. 2: Deconvolution of the carbonyl band within the miscibility domain of plasticized PVC/PMMA blends.

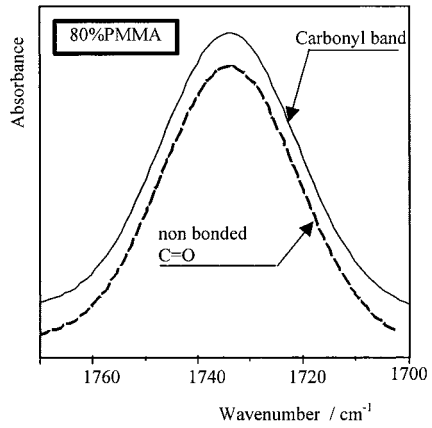

Fig. 3: Deconvolution of the carbonyl band outside the miscibility domain of rigid PVC/PMMA blends.

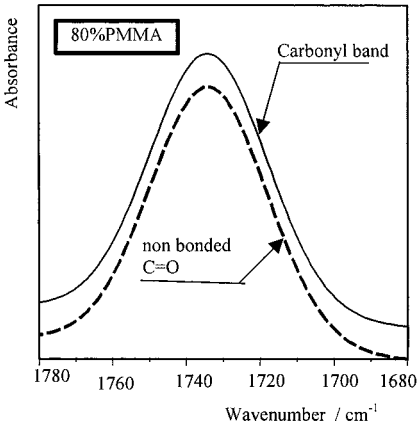

Fig. 4: Deconvolution of the carbonyl band outside the miscibility domain of plasticized PVC/PMMA blends.

Fig. 5 and 6 show the results of thermogravimetric analysis of the rigid and plasticized PVC/PMMA blends, respectively.

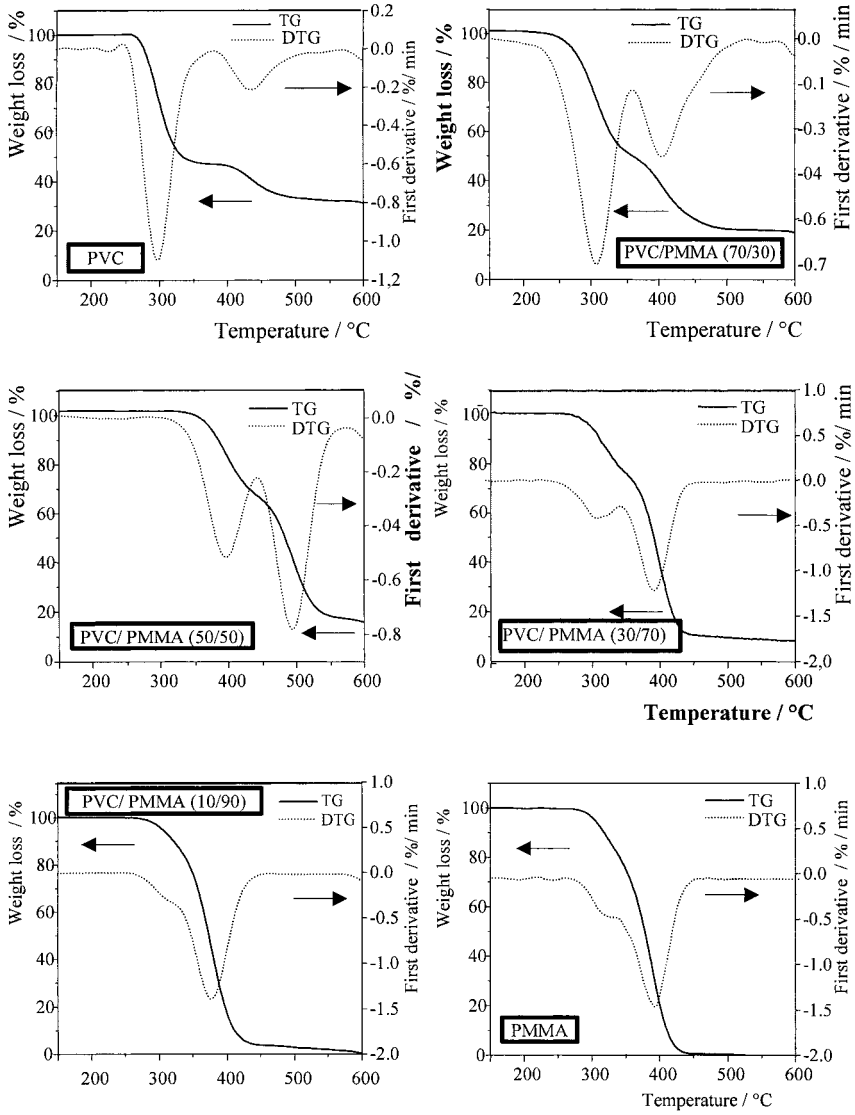

Fig. 5: TG and DTG curves for rigid PVC/PMMA blends.

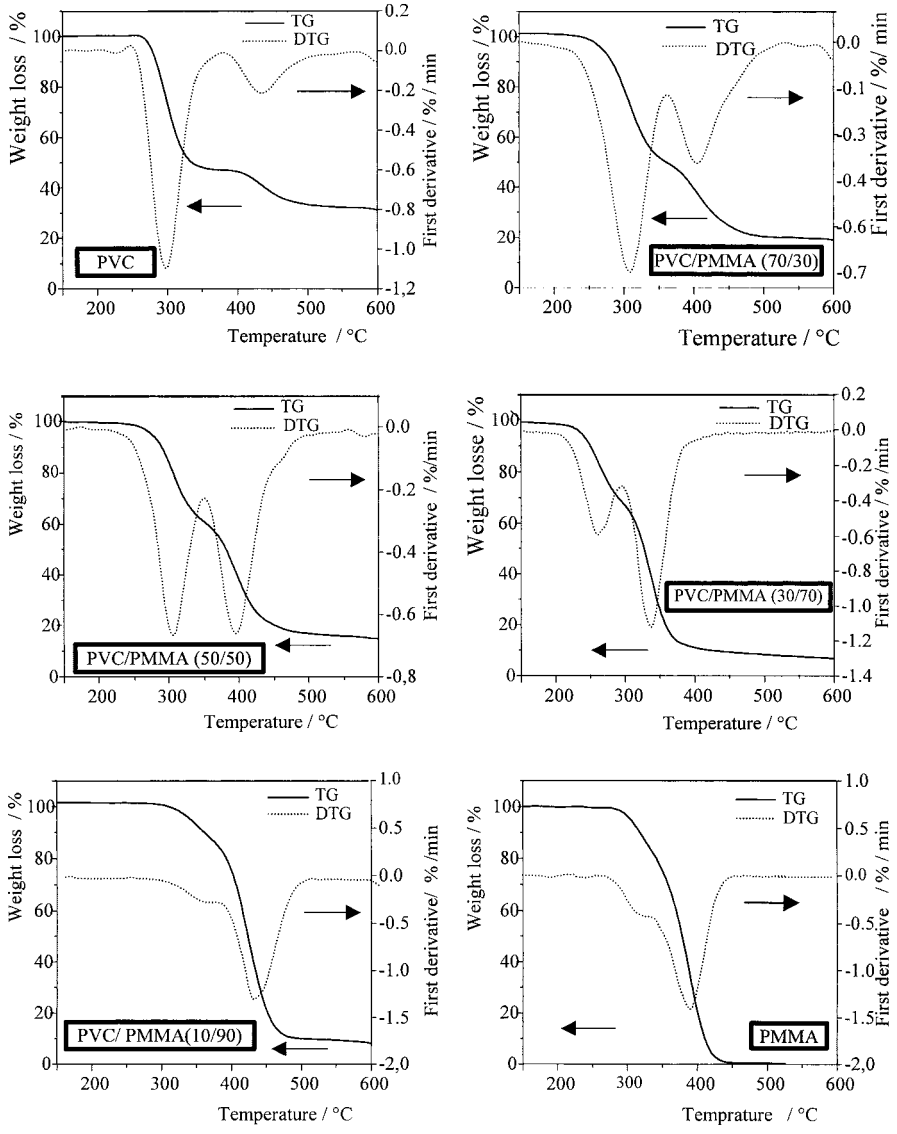

Fig. 6: TG and DTG curves for plasticized PVC/PMMA blends.

Table 3. Results of thermogravimetric analysis of rigid PVC/PMMA blends.

Sample		PVC	70 / 30	50 / 50	30 / 70	10 / 90	PMMA
Weight $loss_{(1)}$	(%)	58	40	30	15	12	100
$Tmax_{(1)}$	(°C)	340	400	395	325	305	395
Weight $loss_{(2)}$	(%)	75	88	78	90	95	-
$Tmax_{(2)}$	(°C)	490	510	490	400	375	-

Table 4. Results of thermogravimetric analysis of plasticized PVC/PMMA blends.

Sample		PVC	70 / 30	50 / 50	30 / 70	10 / 90	PMMA
Weight $loss_{(1)}$	(%)	52	40	30	28	18	100
$Tmax_{(1)}$	(°C)	295	315	305	265	330	385
Weight $loss_{(2)}$	(%)	68	80	78	90	90	-
$Tmax_{(2)}$	(°C)	425	405	395	335	420	-

Weight $loss_{(1)}$ = weight loss at the end of the first step.
Weight $loss_{(2)}$ = total weight loss at the end of the second step.
$Tmax_{(1)}$ and $Tmax_{(2)}$: temperatures of maximum weight loss in the steps 1 and 2, respectively.

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.

Fig. 7 and 8 show the corresponding degradation curves. All the blends are more stable than PVC and the thermal stability increases with increasing the amount of PMMA in the blend.

Furthermore, for a same blend composition, plasticized mixtures showed longer induction times than rigid mixtures (Fig. 9). The induction time in defined as the time before the accelerated DHC occurs. MC NEILL et al.[10, 11] explained the better 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.

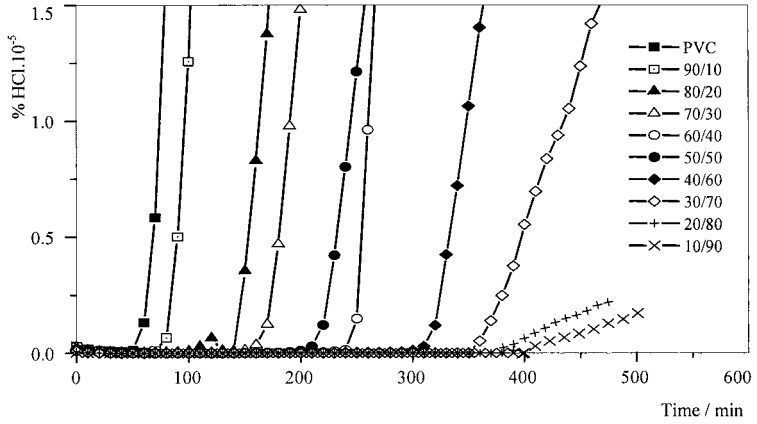

Fig. 7. Dehydrochlorination curves of rigid PVC/PMMA blends at 185 °C in nitrogen.

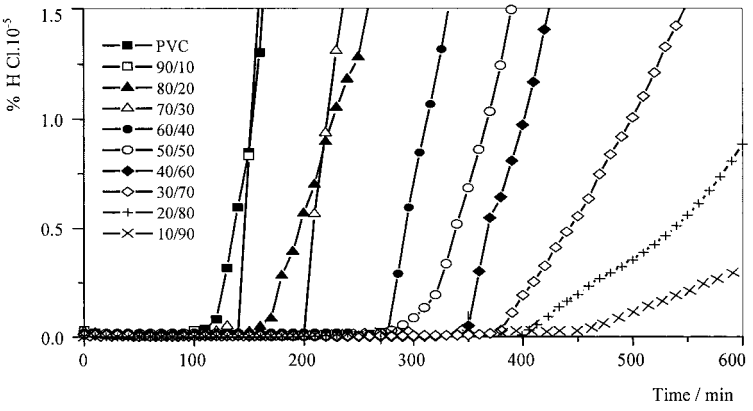

Fig. 8. Dehydrochlorination curves of plasticized PVC/PMMA blends at 185 °C in nitrogen.

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.

Examples of FTIR spectra of degraded samples after purification are shown in Fig. 10 and 11. 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 depolymerisation of PMMA have occurred. However, the relative decrease of the carbonyl band of PMMA at 1730 cm^{-1} which can be related to the depolymerisation became apparent from 100 minutes (Fig. 10) and 180 minutes (Fig.11) of thermal degradation for rigid and plasticized PVC/PMMA (70/30) blends, respectively. These features indicate that chlorine radicals evolved from PVC reacted with the thermal stabilizer present in the blend. When the thermal stabilizer is consumed chlorine radicals attack PMMA which begin to depolymerise.

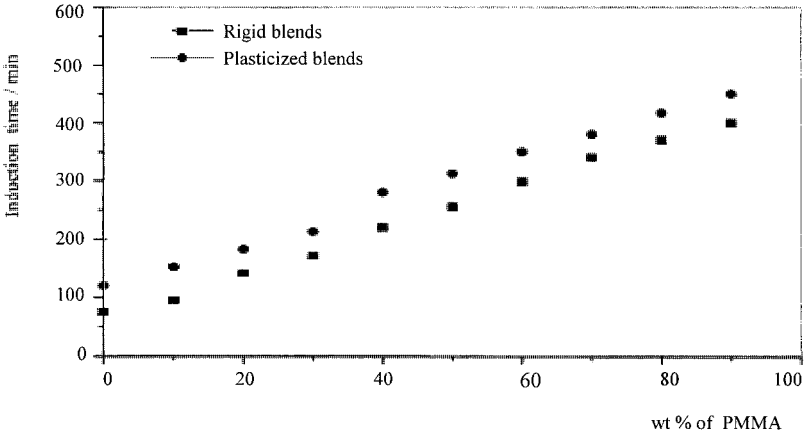

Fig. 9. Variation of the induction time (ti) as a function of the amount of PMMA.

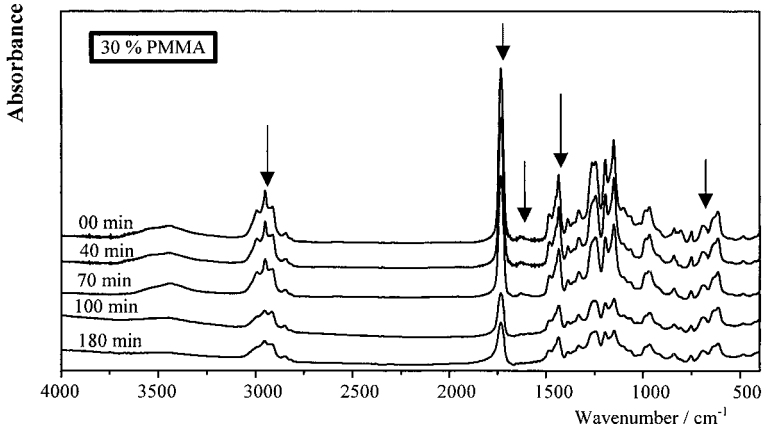

Fig. 10. FTIR spectra of the rigid blend PVC/PMMA (70/30) at various times of degradation at 185 °C.

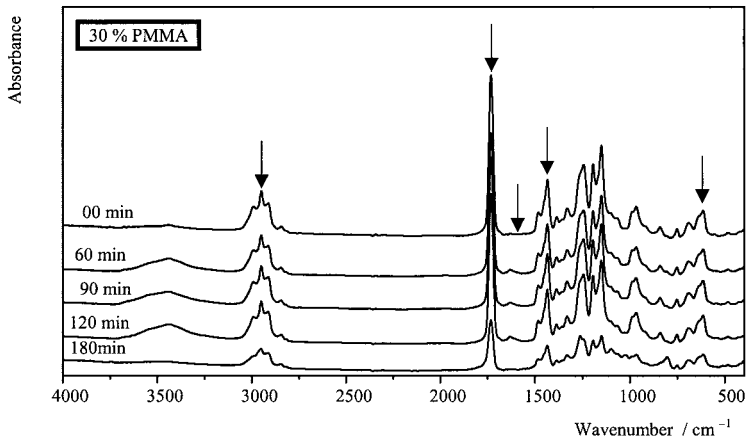

Fig. 11. FTIR spectra of the plasticized blend PVC/PMMA (70/30) at various times of degradation at 185 °C.

All the previous results indicated that the presence of the plasticizer has an important influence on the behavior of the PVC/PMMA blends.

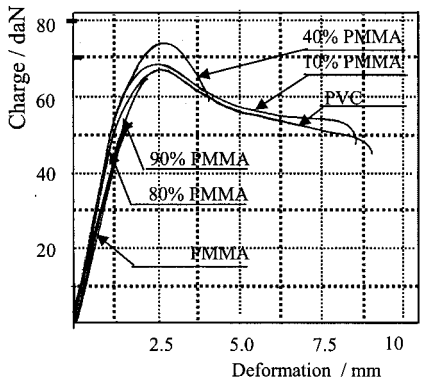

Fig. 12. Tensile curves of rigid PVC/PMMA blends.

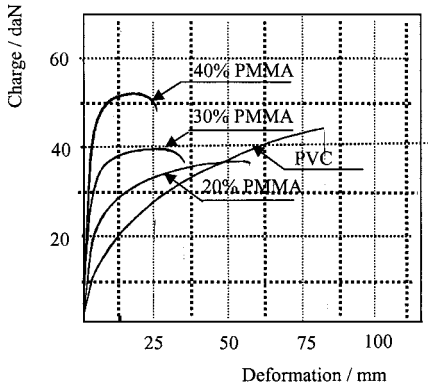

Fig. 13. Tensile curves of plasticized PVC/PMMA blends.

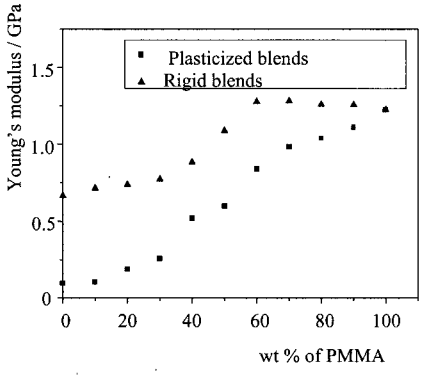

Fig. 14. Variation of Young's modulus with blends composition.

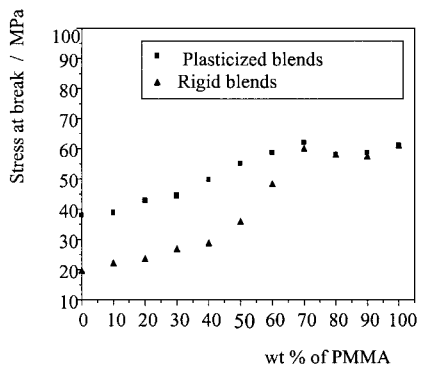

Fig. 15. Variation of stress at break with blends composition.

The mechanical characterization confirmed this feature. Tensile behavior of the various blends which were studied is illustrated in Fig. 12 (without plasticizer) and Fig. 13 (with plasticizer). The comparison between the charge- elongation curves shows that the presence of the plasticizer has modified tensile behavior of PVC/PMMA blends. From the stress-strain curves, Young's modulus (E), which was computed from the initial slope of the curves, stress at break and strain at break were determined and evaluated as a function of the blend composition.

E values obtained for rigid blends are higher than those of plasticized blends (Fig. 14). This feature indicates the diminution of the chains interactions due to the plasticizer.

Fig. 15 shows that the values of stress at break obtained for plasticized blends are higher than those of rigid blends. Furthermore this property presents a maximum corresponding to about 70 wt % of PMMA, decreases slowly after and the values obtained become identical for both rigid and plasticized blends.

Fig. 16 illustrates the variation of strain at break with blends composition. The higher values of strain at break are observed for plasticized blends while very weak values practically constants are observed for rigid blends. From about 70 wt % of PMMA the values obtained become identical for both considered blends.

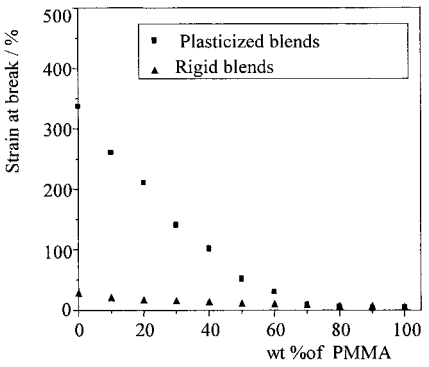

Fig. 16: Variation of strain at break with blends composition.

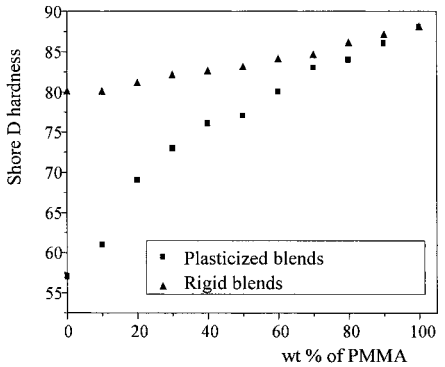

Fig. 17: Variation of hardness with blends composition.

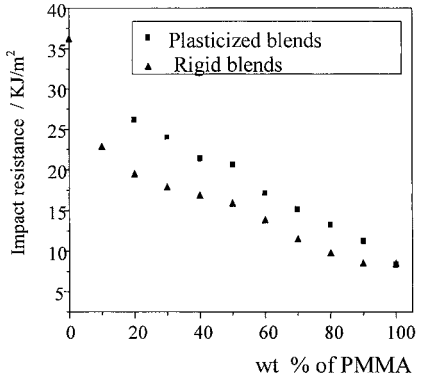

Fig.18: variation of Charpy impact resistance with blends composition.

Shore D hardness is influenced by the rigidity of PMMA (Fig.17). However the presence of the plasticizer decreases it strongly because of the flexibility of the polymeric chains. On the contrary the plasticizer increases the impact resistance's (Fig.18), but globally this property decreases with increasing the amount of PMMA in both considered blends.

Conclusions

The analysis of thermograms showed miscibility up to 50 wt % 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.

Thermogravimetric analysis showed that the weights losses of the blends are lower than those of PVC and PMMA in the first step of degradation indicating that PMMA exerted a stabilizing effect on the degradation of PVC. Dehydrochlorination curves showed that the blends are more stable than PVC and the thermal stability increases with increasing the amount of PMMA in the blend. Furthermore, for a same blend composition, plasticized mixtures showed longer induction times than rigid mixtures.

Young's modulus, stress and strain at break, hardness and impact resistance are dependant on the blend composition and on the presence or the absence of plasticizer. Miscibility of the two polymers seems to have an effect on these properties also. All the obtained results show that a set of mechanical properties can be generated by blending rigid or plasticized PVC with PMMA.

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