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Isothermal and Dynamic Thermogravimetric Degradation of Rigid and Plasticized Poly(Vinyl Chloride)/Poly(Methyl Methacrylate) Blends

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The thermal degradation of rigid and plasticized poly(vinyl chloride) (PVC)/poly(methyl methacrylate) (PMMA) blends was investigated by means of isothermal and dynamic thermogravimetric analysis in a flowing atmosphere of air. For that purpose, blends of variable composition from 0 to 100 wt% were prepared in the presence (15, 30 and 50 wt%) and in the absence of di-(2-ethyl hexyl) phthalate (DEHP) as plasticizer. The thermal degradation of the blends was investigated by isothermal thermogravimetry at 180°C during 120 min. It was found that the main processes are the dehydrochlorination of PVC and depolymerization of PMMA. The dynamic thermogravimetric experiments were carried out in the temperature range of 30–550°C. The results showed that the thermal degradation of rigid and plasticized PVC/PMMA blends in this broad range of temperatures is a three-step process and that PMMA exerted a stabilizing effect on the thermal degradation of PVC during the first step by reducing the dehydrochlorination.

Keywords: blends, DEHP, PMMA, PVC, thermogravimetry

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INTRODUCTION

Poly(vinyl chloride) (PVC), one of the oldest polymers, enjoys the largest production in commercial scale because of its extremely varied applications in different branches of industry. However, one of the problems associated with the processing and use of PVC is its low thermal stability. It starts degrading above the glass transition temperature (ca. 80°C) by initiation (random at normal repeat units and at structural defects) followed by fast zip elimination of HCl and, at the same time, formation of conjugated double bonds (polyenes) in the backbone of the polymer. The dehydrochlorinated chains take part in the secondary processes, which result in volatile aromatic and aliphatic compounds [1,2]. Thermo-oxidative degradation of PVC is more complex than pyrolysis; not only the thermal degradation but also the oxidation of polyenes must be considered. Due to the difficulties in the identification of primary products of degradation, the suggested reaction scheme is more or less general: the mechanism includes oxidation of normal structures via radicals and peroxy radical formation [3,4].

Poly(methyl methacrylate) (PMMA) is a hard, rigid, transparent and rather fragile polymer, and widely used. It is known that PMMA depolymerizes almost exclusively to the monomer when heated. The degradation is a radical depolymerization process involving both chain end-group activation and random scission initiation of monomer elimination [5].

Polymer blends generally undergo the same degradation reactions as the original polymers, but in most cases the rate of degradation changes, depending on the nature of polymer added, on the degree of miscibility of the polymer pair or on the interaction of degradation products. McNeill et al. [6–8] have found that PMMA is slightly less stable and gives monomer at temperatures corresponding to PVC dehydrochlorination (DHC). Braun et al. [9,10], studying the thermal degradation of PVC with various polymethacrylates, have shown that longer n-alkyl ester groups and higher concentrations of the respective polymethacrylate exhibit some stabilization of PVC. More recently, Braun et al. [11] synthesized copolymers based on methacrylates and investigated them as co-stabilizers for PVC. They found that these polymers are capable of improving the induction time of PVC dehydrochlorination.

In previous works, the thermal [12,13] and thermo-oxidative [14] dehydrochlorination of rigid and plasticized PVC/PMMA blends were studied by measuring the amount of HCl released from PVC by a continuous potentiometric method. In both cases, 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.

In order to understand the role of PMMA and plasticizer on the thermal degradation of rigid and plasticized PVC/PMMA blends, studies on isothermal and dynamic thermodegradation of these blends are carried out and reported in the present paper. Since the blends are generally submitted to the effects of heat and air during both processing and use, a good knowledge of their thermo-oxidative behavior is very important. For that purpose, blends of variable composition from 0 to 100 wt% were prepared in the presence (15, 30 and 50 wt%) and in the absence of di-(2-ethylhexyl)phthalate (DEHP) as plasticizer.

EXPERIMENTAL

Materials

Commercial grades of PVC, PMMA and additives listed in Table 1 were used as received. The K value of PVC is 67 according to the DIN 53-726; $\rho(\text{PVC}) = 1.54 \text{ g/cm}^3$; $\rho(\text{PMMA}) = 1.18 \text{ g/cm}^3$; $M_n(\text{PVC}) = 89,700$; $M_n(\text{PMMA}) = 57,900$.

Blends of PVC and PMMA of variable compositions from 0 to 100 wt% were prepared in the presence of 0, 15, 30 and 50 wt% of DEHP, 1 wt% of lubricant and 3 wt% of heat stabilizer. The amounts of the three additives were added according to the amount of PVC in the blend. Melt mixing was performed at 175°C for 8 min in a two-roll mill. The blends were then hot compressed at 180°C for 3 min under a pressure of 200 kN.

Isothermal Thermogravimetric Analysis

The isothermal degradation of the blends was carried out thermogravimetrically by using an ATG (Q500) instrument at 180°C for 120 min

TABLE 1 Compounds Used in this Study

Compound	Source
PVC 4000M	ENIP-Skikda (ALGERIA)
PMMA	BASF (GERMANY)
Ba/Cd/Zn (heat stabilizer)	HENKEL (GERMANY)
Stearic acid (lubricant)	HENKEL (GERMANY)
Di-(2-ethylhexyl)phthalate(plasticizer)	BASF (GERMANY)

under synthetic air flow of 90 ml/min on 15 mg of each sample. The samples were heated at a rate of 100°C/min from the starting temperature (30°C) to the temperature of isothermal degradation. This test was carried out on rigid and plasticized blends with 15 and 50 wt% of DEHP.

Dynamic Thermogravimetric Analysis

Thermogravimetric (TG) analysis was performed on the polymeric blends by using an ATG (Q500) instrument. The samples ranging between 10 and 15 mg were heated under air flow (90 ml/min) from room temperature to 550°C on the basis of the following heating rates: from room temperature to 180°C at 20°C/min, from 180 to 230°C at 1°C/min, and from 230 to 550°C at 5°C/min. These heating rates were selected to detect the weight loss in various temperature intervals. The slow heating rate (and thus longer heating time) increases the phase aggregation tendencies in blends. When the polymer blends are degraded at higher heating rates (giving less time to degradation) the phase segregation which depends upon diffusion process does not give the same phenomenon in the case of low heating rates.

Two experiments were performed for each sample to ensure the consistency and repeatability of the results. No significant deviations were observed in the shape of the TG plots. The results presented here were reproducible and the temperature and mass loss deviations were within the maximum range of $\pm 2\%$.

RESULTS AND DISCUSSION

Isothermal Thermogravimetric Study

The TG curves of thermo-oxidative isothermal degradation of PVC/PMMA blends are given in Figure 1. All the blends exhibited lower mass loss than PVC but higher loss than PMMA. The mass loss depends on the composition of the blend: it decreases with the amount of PMMA and increases with the amount of plasticizer as is clearly shown in Table 2. Globally, the mass loss doesn't exceed 3% for rigid blends and 18% for plasticized ones. On the other hand, the initial rates of the mass loss which were determined from the linear part of the thermogravimetric curves of Figure 1 follow the same trend as the mass loss (Table 3). The greater the level of PMMA, the lower is the initial rate of the mass loss. The greater the level of plasticizer, the greater is the initial rate. All these features indicate that both DHC of PVC and depolymerization of PMMA occurred, and that the

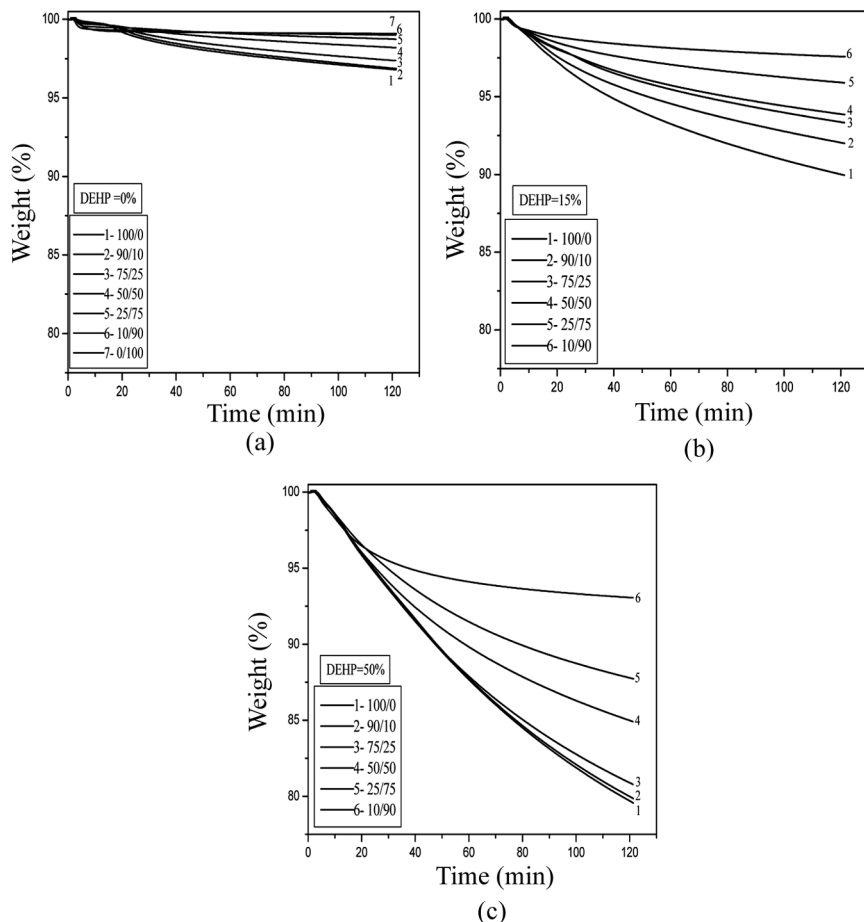


FIGURE 1 Isothermal TG curves of rigid and plasticized PVC/PMMA blend at 180°C.

polymers and their products of degradation interact strongly. Indeed, the initial formation of chlorine radicals destabilizes PMMA, which gives monomer at abnormally low temperatures. These effects can be explained in terms of chlorine radical attack on the PMMA, resulting in chain scissions and depolymerization of the polymer. Thus, the chlorine radical fails to form HCl whose autocatalytic effect on DHC of PVC is well known. On the other hand, even if some HCl is produced, it fails to catalyze the process of subsequent degradation as it reacts with the ester groups of PMMA, giving rise to anhydride rings which act as locking groups, reducing the zip length of depolymerization and

TABLE 2 Isothermal Mass Loss of Rigid and Plasticized PVC/PMMA Blends after 120 min at 180°C

PVC/PMMA	Mass loss (Δm) (%)		
	0% DEHP	15% DEHP	50% DEHP
100/0	2.86	7.98	17.72
90/10	2.75	8.59	17.38
75/25	2.23	5.20	16.39
50/50	1.42	4.65	12.35
25/75	0.73	2.91	9.80
10/90	0.33	1.45	4.15
0/100	0.15	–	–

thus stabilizing the chain. Moreover, the unzipped monomer (MMA) is considered to be a very good radical scavenger and thus scavenges the chlorine radicals immediately as they are formed. All of these mechanisms were detailed by Chakrabarti et al. [15]. In this way, there is a mutual stabilizing effect whereby PVC is stabilized by PMMA in the blend by not allowing the chlorine radical to form hydrogen chloride and subsequently not permitting the HCl, when formed, by forming an anhydride type of structure.

These results are in accordance with a previous work where the thermo-oxidative DHC of the same rigid and plasticized PVC/PMMA blends was measured at the same temperature [14]. We found that all, the blends were more stable than PVC and the initial rate of DHC decreased with increasing the amount of PMMA. Moreover, we found also that the initial rate of DHC decreased with the amount of DEHP while the induction time increased. The fact observed in

TABLE 3 Initial Rate of Weight Loss of Rigid and Plasticized PVC/PMMA Blends at 180°C

PVC/PMMA	Initial rate of weight loss %/min		
	0% DEHP	15% DEHP	50% DEHP
100/0	0.048	0.159	0.230
90/10	0.043	0.140	0.227
75/25	0.035	0.110	0.225
50/50	0.026	0.103	0.208
25/75	0.023	0.093	0.183
10/90	0.017	0.077	0.160
0/100	0.013	–	–

the present work that the mass loss increased with the amount of plasticizer is probably related to the greater free volume in the polymer matrix, which favors the mobility, and the effects of the degradation products which are formed. These results suggest that depolymerization of PMMA increased with the level of plasticizer.

The very low value of mass loss obtained for PMMA alone (0.15%) as shown in Table 2 corresponds to the volatilization of some polymerization residue. Depolymerization of PMMA doesn't occur at 180°C.

Dynamic Thermogravimetric Study

The influence of PMMA in a PVC matrix on the thermal stability of rigid and plasticized PVC/PMMA blends was investigated by dynamic thermogravimetric analysis (TGA) from 30 to 550°C at various heating rates. The thermograms are given in Figure 2. Except for PMMA, the thermal decomposition temperatures involved at least three steps of degradation as measured from the peaks observed from the first derivative of thermogravimetric (TG) curves. The corresponding data are given in Table 4. The results showed that thermal decomposition of PMMA occurred at 303°C by statistical chains scissions followed by depolymerization and liberation of the pure monomer. A 100% weight loss is attained. Concerning rigid and plasticized PVC, the first stage corresponds to the dehydrochlorination of the polymer and the most abundant volatile product is HCl. The mass loss increased with the level of plasticizer as shown in Table 4. The free volume induced by the presence of DEHP allows a better diffusion of the HCl produced and leads to an increase of its autocatalytic effect on PVC DHC, which results in a more rapid consumption of the heat stabilizer. These facts explain the increase of the speed of maximal weight loss with the level of DEHP as shown in Table 4. As DHC of PVC results in the formation of conjugated double bonds, the second step of the thermal degradation represents the oxidation of polyenes to compounds of lower molecular masses. It is accompanied by the plasticizer evaporation (DEHP vaporizes at 323°C) in the case of plasticized PVC, and other low-temperature volatile components in the case of rigid PVC. The plasticizer evaporation involves the creation of voids around the chlorine atoms, making their release and diffusion easier. The third step corresponds to further oxidation which leads to the production of additional volatile compounds. Our results are in agreement with those of Matuschek et al. [16] who reported the release of phthalate-based plasticizer along with the release of HCl from PVC in the range 320–340°C. Benes et al. [17] observed the release of DEHP, HCl and CO₂ by simultaneous TG/FTIR in the range 200–340°C.

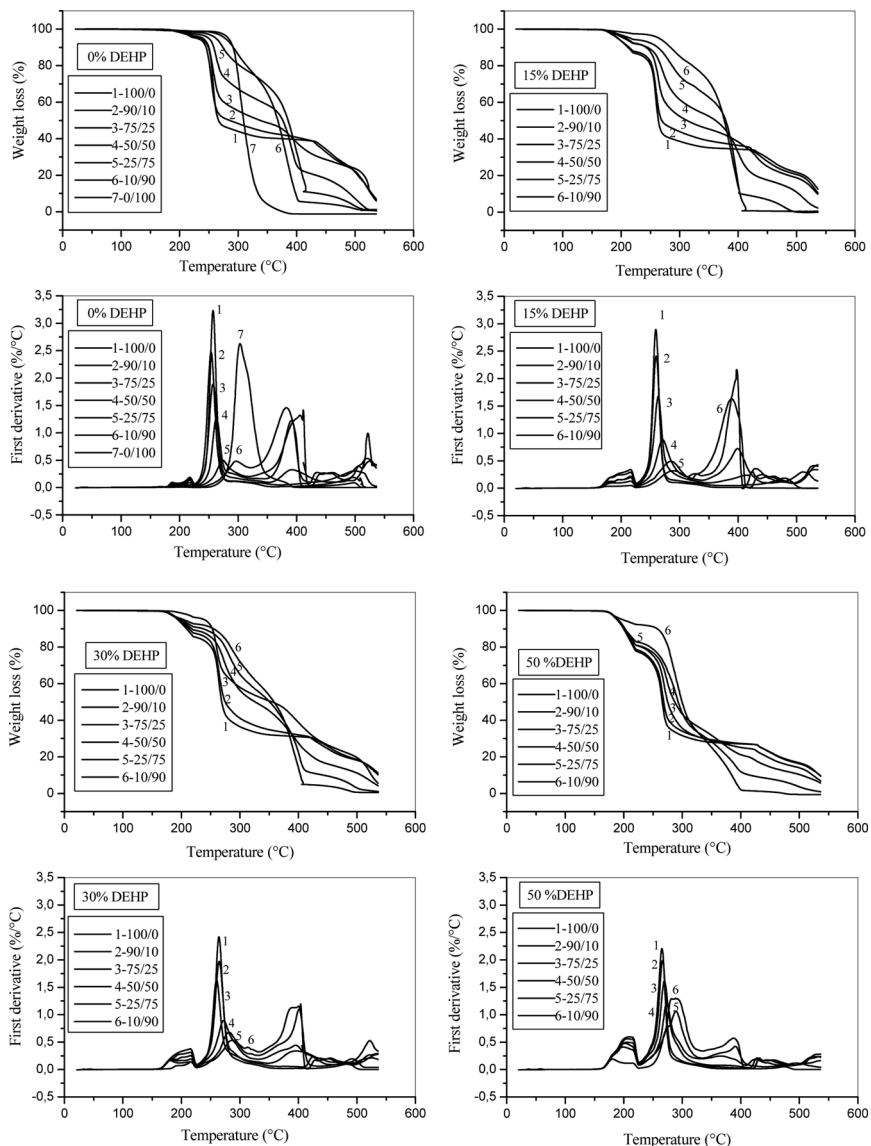


FIGURE 2 Weight loss and weight loss derivative of rigid and plasticized PVC/PMMA with various concentrations of DEHP.

The addition of PMMA to the blends stabilized PVC in the first step of thermal degradation: the weight loss, the temperature of maximum weight loss and the speed of maximal weight loss decreased with the

TABLE 4 Results of Thermogravimetric Analysis of Rigid and Plasticized Blends

PVC/PMMA/DEHP	Stage 1			Stage 2			Stage 3			W _{total}
	W ₁	T _{max}	S _{max}	W ₂	T _{max}	S _{max}	W ₃	T _{max}	S _{max}	
100/0/0	4.65	217.9	0.18	53.08	254.1	3.20	27.85	439.4	0.24	85.58
90/10/0	4.37	217.1	0.15	51.78	257.2	2.45	30.02	430.2	0.31	86.17
75/25/0	3.69	216.3	0.13	47.40	257.3	1.87	37.87	393.5	0.35	88.96
50/50/0	2.29	216.1	0.09	40.93	263.1	1.24	55.58	392.4	0.93	98.80
25/75/0	1.31	216	0.05	39.02	273.1	0.49	59.27	390.7	1.31	99.60
10/90/0	0.56	215	0.02	35.60	296.4	0.47	63.64	382.2	1.46	99.80
0/100/0	–	–	–	–	–	–	100	303.2	2.61	100
100/0/15	13.49	216.4	0.33	51.18	259.4	2.86	14.78	462.5	0.22	79.45
90/10/15	12.46	215.8	0.28	48.38	259.4	2.38	23.86	430.2	0.30	84.70
75/25/15	8.05	215.6	0.21	46.69	263.6	1.66	31.81	424.2	0.33	86.55
50/50/15	7.86	215.3	0.19	39.35	270.7	0.88	39.85	399.2	0.71	87.06
25/75/15	5.69	215.2	0.12	36.51	285.4	0.48	53.55	397.9	1.22	95.75
10/90/15	2.21	215	0.05	33.35	288.8	0.32	61.61	388.4	1.43	97.17
100/0/30	14.96	216.38	0.37	47.96	264.1	2.40	14.67	464.2	0.20	77.59
90/10/30	12.60	216.38	0.31	45.56	264.9	1.95	22.76	450.8	0.23	80.92
75/25/30	10.64	216.38	0.25	38.45	272.5	1.61	30.71	430.5	0.27	81.19
50/50/30	8.93	215.62	0.19	36.99	281.5	0.89	37.88	401.1	0.44	83.80
25/75/30	7.12	215.62	0.16	35.53	285.7	0.67	46.19	400.2	1.09	88.84
10/90/30	3.76	215.62	0.14	32.37	288.9	0.53	54.67	389.6	1.13	90.80
100/0/50	24.01	210.77	0.58	44.01	265.6	2.16	13.47	431.3	0.18	81.49
90/10/50	21.89	209.4	0.53	46.18	266.3	1.96	13.55	430.1	0.20	81.62
75/25/50	19.63	207.1	0.49	49.15	270.1	1.59	15.14	428.3	0.22	83.92
50/50/50	19.20	202.3	0.47	51.49	274.1	1.29	20.55	424.7	0.25	91.24
25/75/50	17.28	199.5	0.41	53.62	289.8	1.19	27.56	390.0	0.47	98.46
10/90/50	7.43	181.1	0.18	60.83	293.1	1.05	31.05	387.9	0.56	99.31

W: weight loss (%).

T_{max}: Temperature of maximum weight loss (°C).

S_{max}: Speed of maximal weight loss (%/min).

W_{Total}: Total of weight loss in stages 1, 2, and 3 (%).

amount of PMMA as shown in Table 4. These same parameters increased with the amount of DEHP. These results are in agreement with those obtained in the previous isothermal gravimetric study. They confirm that both DHC of PVC and depolymerization of PMMA occurred, and that the two polymers exerted a mutual stabilizing effect. It is to be noted that this step of degradation was conducted at two heating rates: from room temperature to 180°C at 20°C/min and from 180 to 230°C at 1°C/min. This second slow heating rate leads to long heating times and allows a good investigation of the degradation reactions. In the second step of thermal degradation, the values

of weight loss, temperature of maximum weight loss and speed of maximal weight loss are higher than that obtained in the first step. However, the weight loss decreased with the amount of PMMA, while the temperature of maximum weight loss increased, which confirms that although both DHC of PVC and depolymerization of PMMA are accelerated by temperature, the two polymers still exert a mutual stabilizing effect. During this second step the scission of polyenes also occurred, leading to the formation and loss of low hydrocarbons of linear or cyclic structure [18].

In the third and last step of thermal degradation, which was conducted at a heating rate of 5°C/min, the weight loss and the speed of maximum weight loss increased with the amount of PMMA while the temperature of maximum weight loss decreased. All these features indicate that the thermal degradation is accelerated and that the oxidation is almost complete.

CONCLUSIONS

The study of the TG isothermal oxidative degradation at 180°C of rigid and plasticized PVC/PMMA blends showed that the mass loss decreases with the amount of PMMA and increases with the amount of plasticizer. Both DHC of PVC and depolymerization of PMMA occurred and the two polymers exerted a mutual stabilizing effect.

The investigation of thermal degradation of the same blends by dynamic TG analysis, from 30 to 550°C, showed three steps. The weight loss, the temperature of maximum weight loss and the speed of maximum weight loss in each step are dependent on the blend composition and on the amount of plasticizer.

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