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THERMAL AND PHOTOCHEMICAL STABILITY OF POLY(METHYL METHACRYLATE) AND ITS BLENDS WITH POLY(VINYL ACETATE)

A. Kamińska and M. Świątek

Faculty of Chemistry, N. Copernicus University, 87-100 Toruń, Poland

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Abstract

An investigation of the thermal stability of poly(methyl methacrylate) (PMMA) blends with poly(vinyl acetate) (PVAc) revealed that PVAc acts as a stabilizer as concerns thermal and photochemical degradation when the processes take place in air. The temperatures of decomposition of these blends are higher than that of pure PMMA. The efficiency of photodegradation and photooxidation in the blends is lower than that of pure PMMA.

Keywords: polymer blends, thermal stability, photooxidation, poly(methyl methacrylate) PMMA, poly(vinyl acetate) PVAc

Introduction

Poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) have similar thermal stabilities, but different photochemical stabilities. PMMA is one of the polymers most resistant to UV radiation. PVAc does not have such a great resistance [1–14].

Even though the thermal and photochemical processes of pure individual polymers have been adequately investigated, their blends may exhibit stability behaviour different from the summation of these properties of the individual polymers [15–18].

It is known that the components of polymer blends may mutually stabilize [15–18] or sensitize [19–23] one another or one component may be stabilized at the expense of the second one [24].

The results of most of these investigations were obtained for blends with a considerable (20–50%) content of the second component.

Our previous studies of PVC blends with modifying copolymers ABS, MBS, VC/VAC and MMA/MA, or of PS blends with PMMA, PVC and PB, showed that the effects of the second component on the thermal and photochemical stabilities of polymer blends depend not only on the nature of the modifier, but also on its concentration [25–27].

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The aim of this work was to investigate the effects of small contents of PVAc in PMMA on its thermal and photochemical stabilities, and also the influence of photochemical transformations on the thermal parameters of these samples.

Experimental

PMMA with limiting viscosity number (LVN)=80.4 cm^3/g, and PVAc with LVN=35 cm^3/g were used after purification by precipitation of the polymers from benzene solution with methanol. Samples for investigation were prepared in the form of films 0.020 mm thick, from PMMA and from its blends with 1–20% PVAc. They were obtained by solvent evaporation from a 2% solution of the polymer poured onto glass plates. The films were dried at room temperature, and again dried under reduced pressure to constant mass.

The films were irradiated in air at room temperature by means of a Philips TUV-30 mercury lamp, which emitted light mainly of 253.7 nm wavelength. Parts of films were heated at 200°C in air.

The IR spectra of films before and immediately after irradiation or heating were recorded with a UR-10 spectrophotometer (Carl Zeiss, Jena). The IR spectra were analysed by using a spectroscopic computer system (KSR-4100 Specord 75 IR). From these results, the ratio of the absorbance of the OH band, A_{3420}, to the absorbance of the standard deformation band of the CH_2 group, A_{1435}, was calculated. The changes in absorbance of this band after irradiation or heating were determined.

The LVN of benzene solutions of the polymers were determined at 20±0.05°C with an Ubbelohde viscometer.

Thermal analyses were carried out in a Paulik-Paulik-Erdey derivatograph in nitrogen or in air atmosphere, at a heating rate of 6°C min^{-1} up to 600°C. From the thermal curves, the temperatures of the starting points of the total decomposition of the polymers (T_o) and the temperatures of the end decomposition (T_k) were evaluated.

Results and discussion

The thermal decompositions of PMMA and PVAc in nitrogen atmosphere begin at T_o=260°C. The end of this process is at T_k=435°C for PMMA, and at 530°C for PVAc (Table 1).

The onset of decomposition of PMMA/PVAc blends begins only at slightly lower T_o and does not indicate the mutually destabilizing effect of these polymers.

T_k for the blends is higher than T_k for pure PMMA, and increases with increase of the content of PVAc (with higher T_k) in PMMA.

Again, such changes do not suggest the thermal interaction of these polymers under these conditions.

UV irradiation causes a drastic decrease of T_o for pure PMMA and PVAc measured in nitrogen atmosphere (Table 1). For PMMA/PVAc blends, these

Table 1 Thermal parameters characterizing PMMA, PVAc and PMMA/PVAc blends determined in nitrogen atmosphere

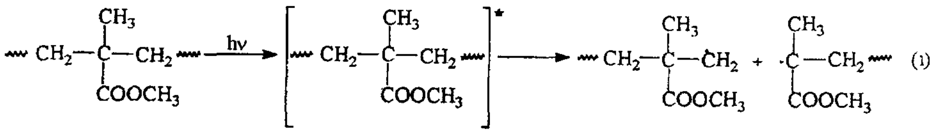
Amount of PVAc/ in PMMA%	Thermal parameters before irradiation		Thermal parameters after 8 h irradiation	
	T_o /°C	T_k /°C	T_o /°C	T_k /°C
0	260	435	165	460
1	245	440	265	445
5	250	460	250	450
10	250	465	240	460
20	250	465	240	460
100	260	530	240	480

Table 2 Changes of LVN caused by UV-irradiation in PMMA and its blends with PVAc

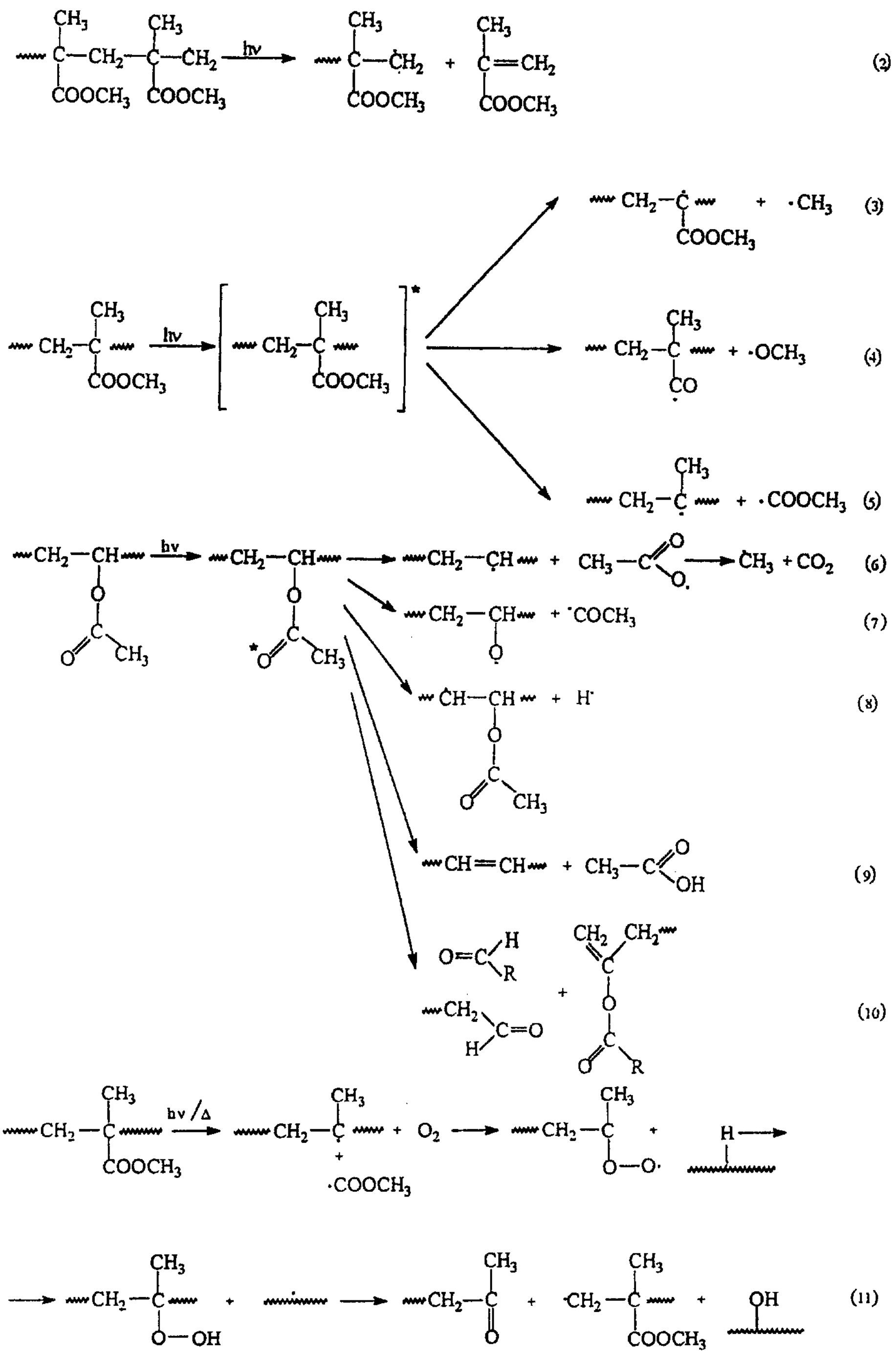
Amount of PVAc/ in PMMA%	–Δ LVN after UV irradiation	
	1 h	2 h
0	46.0	58.0
1	42.5	58.0
5	42.4	53.5
10	34.8	48.0
20	31.2	40.0

changes are only insignificant and are within the limits of excremental error. This is also the case for T_k of the blends, but T_k increases by about 25°C for pure PMMA and decreases by about 50°C for PVAc.

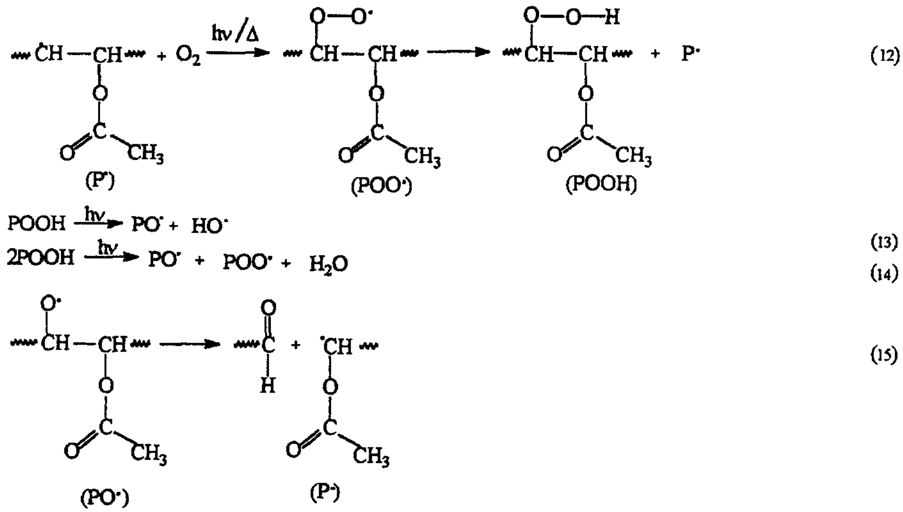
These results suggest that photochemical transformations in PMMA and PVAc samples occur with greater efficiency than in their blends. This especially concerns those processes which may decrease the thermal stability of polymers: polymer degradation with bond scission in the main chain (reactions 1, 2 and 10) [28–33], and the formation of radicals and macroradicals, which causes changes in the structure and chemical composition of polymer macromolecules (reactions 3–9) [34–36].



Reactions 1



Reactions 2–11



$$POOH \xrightarrow{h\nu} PO^{\cdot} + HO^{\cdot} \quad (13)$$

$$2POOH \xrightarrow{h\nu} PO^{\cdot} + POO^{\cdot} + H_2O \quad (14)$$

Reactions 12–15

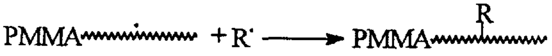
These suggestions were confirmed by the results of viscosity measurements. They reveal the rapid decrease of the LVNs of PMMA samples during UV irradiation, and the smaller changes of LVN in PMMA/PVAc blends (Table 2). Photooxidation occurs with lower efficiency in PMMA/PVAc blends than in pure unmixed PMMA (Table 3).

Table 3 Changes of concentration of OH groups caused by UV-irradiation in PMMA and its blends with PVAc

Amount of PVAc/ in PMMA%	Δ [OH] after UV-irradiation 2 h	Δ [OH] after UV-irradiation 4 h
0	0.0285	0.0538
1	0.0160	0.0272
5	0.0090	0.0223
10	0.0101	0.0292
20	0.0173	0.0402

Insignificant thermal stability changes caused by UV irradiation in PMMA/PVAc blends point to the mutual photostabilization of these polymers.

This stabilizing mechanism probably results form the quenching of PMMA macroradicals by radicals $R^{\cdot}$($\dot{C}H_3$, $\dot{O}COCH_3$, $\dot{C}OCH_3$ $\dot{O}H$ and $\dot{H}$) earlier formed with less stable PVAc. Especially mobile radicals displaced in the mass of the polymer may take part effectively in this reaction:



$$PMMA\!\sim\!\sim\!\dot{}\!\sim\!\sim + R^{\cdot} \longrightarrow PMMA\!\sim\!\sim\!\overset{R}{|}\!\sim\!\sim$$

Thermal analysis in air atmosphere demonstrates an increase in the T_o of PMMA in the presence of PVAc (Table 4).

Table 4 Thermal parameters characterizing PMMA, PVAc and PMMA/PVAc blends determined in air atmosphere

Amount of PVAc/ in PMMA%	Thermal parameters before irradiation		Thermal parameters after 8 h irradiation	
	T_o / °C	T_k/ °C	T_o / °C	T_k/ °C
0	225	380	210	520
1	260	380	230	540
5	250	385	210	560
10	240	560	220	550
20	260	540	240	560
100	260	510	210	440

An appreciable increase of T_o, by about 35°C, was observed in the blend with a 1% content of PVAc. Further increase of the content of this polymer in the PMMA/PVAc blends did not have a distinct effect on T_o.

This suggests that in air atmosphere PVAc has a stabilizing effect on PMMA, and that 1% of PVAc is sufficient to cause this effect. A similar suggestion arises from the efficiency of photooxidation (Table 3). It can be seen that a 1–5% content of PVAc more effectively hampers this process than a higher content of this polymer in PMMA/PVAc blends.

T_k for the blends is higher than the T_k of pure PMMA or PVAc. This again suggests that PMMA acts as a thermal stabilizer of PVAc under these conditions, i.e. in air atmosphere and when the PVAc content in the PMMA/PVAc blend is 10%.

The thermal parameters in air atmosphere of UV-irradiated samples reveal a decrease in T_o and an increase in T_k (Table 4). Such changes may be caused by thermal oxidative degradation, which in air atmosphere may additionally occur besides the normal degradation and photooxidative degradation which take place before the heating of the samples during their UV irradiation (reactions 11–15). In this situation, the efficiency of chain scission increases, and as final result T_o decreases. The $C=O$, OH and COOH groups formed in this oxidation require a higher energy for their decomposition, which explains the increase in T_k for most of the samples.

The values of the thermal parameters (Table 4) suggest that these reactions occur with great efficiency after activation of the polymers by UV radiation.

It can be seen from Tables 1 and 4 that the temperatures of thermal degradation T_o of PVAc and PMMA/PVAc blends are independent of the atmosphere, but T_o for PMMA is clearly higher in nitrogen atmosphere than in air. This may suggest that PVAc hampers all those processes in which PMMA chains react

Table 5 Changes of C=O and OH groups concentration in PMMA and its blends with PVAc after heating at 200°C

Amount of PVAc in PMMA/%	Changes of $A_{C=O}/A_{CH_2}$ after heating 1 h	8 h	A_{OH}/A_{CH_2} after heating 1 h	8 h
0	–0.5613	–1.0292	+0.0158	–0.0013
1	–0.1799	–0.1298	+0.0169	+0.1091
5	–0.0409	–0.0129		
10	+0.3604	+0.1945	+0.0933	+0.1018
20	+0.1457	+0.4197	+0.0923	+0.1343

with O_2. These suggestions may be confirmed by the results of the IR analysis of samples annealed at 200°C in air (Table 5).

The negative changes in C=O group concentration (Table 5) suggest that the process of thermal destruction of PMMA involving fission of the C=O groups in hampered by PVAc.

Conclusions

In air atmosphere, PVAc acts as a thermal stabilizer of PMMA.

Both polymers in PMMA/PVAc blends undergo mutual photostabilization.

PVAc hampers the thermal destruction of PMMA, and its photodegradation and photooxidation.

A small amount (1–5%) of PVAc in PMMA/PVAc blends hampers the oxidative processes and thermal degradation with greater efficiency than do higher contents.

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