

## **THERMAL ANALYSIS IN STUDIES OF PHOTOCHEMICAL TRANSFORMATIONS IN PVC**

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The effects of photochemical processes in PVC in response to UV irradiation at 253.7 nm on its thermal stability were investigated. It was found that small differences in the efficiency of the photochemical processes taking place in the PVC can be recorded in the thermal measurements, and that photodehydrochlorination lowers the temperature of thermal dehydrochlorination, while photooxidation and crosslinking increase the temperature of complete decomposition of this polymer.

Polyvinyl chloride (PVC) is a polymer with poor thermal and photochemical stability. The thermal decomposition of PVC is strongly affected by the structure of the polymer chains. A decrease in the temperature of dehydrochlorination is caused by fragments of polymer resulting from head-to-head linkages [1, 2]. The number of length of the branches also apparently affect the thermal stability of PVC [3–9]. This is particularly so for branches with chlorine atoms at tertiary carbon atoms [5, 6]. A negative effect on the thermal stability of this polymer is exerted by unsaturated intramolecular bonds,  $\beta$ -chloroalkyl groups, double bonds at the chain ends, and groups containing oxygen atoms [10–17]. The effects of the above factors are not always explicit, and the results are often controversial [18, 19]. This is certainly caused by comparison of the results obtained for model low molecular substances with those for different brands of PVC in which the contents of particular groups and defects can be quite different, due to the different conditions of production. The properties may also change in the course of use; for instance, UV irradiation leads to changes in the molecular weight of the polymer, and also to changes in the structure of its chains, causing the formation of new crosslinks, branching, double bonds, conjugated double bonds, carbonyl and hydroxyl groups. The efficiency of photochemical processes is usually low, because of the limited penetration of UV radiation into the polymer and because all the above processes occur only in the thin surface layer.

The aim of our study was to check the possibility of application of thermal analysis for observation of the changes caused by UV radiation in PVC, for determination of the effects of photooxidation, crosslinking and the formation of

double bonds in PVC on its thermal stability, and for evaluation of the influence of small differences in the efficiency of the photochemical processes on the values of the thermal parameters.

In order to differentiate the efficiency of photochemical processes in PVC films under the same irradiation conditions, thin films of PVC with the addition of 1–5% of polystyrene (PS) were prepared. Even at low contents in PVC samples, PS, known as one of the polymers that are more resistant to UV radiation, might influence the efficiency of photochemical processes occurring in them.

### Experimental

Samples of PVC S-60 with  $M_v = 43,300$  g/mol and its blends with 1–5% PS with  $M_v = 360,000$  g/mol were prepared in the form of films about 2.5 nm thick [19].

The films were irradiated in air at room temperature using a Philips TUV-30 mercury lamp, which emitted light of mainly 253.7 nm wave length.

Thermal analyses were carried out with an OD derivatograph in air. Two different peaks in the DTG and DTA curves allow determination of  $T_1^0$ , the temperature of the starting point of dehydrochlorination;  $T_1^{\max}$ , the temperature of the maximum rate of this reaction;  $m_1$ , the mass decrement in this reaction;  $T_2^0$ , the temperature of the starting of total decomposition of PVC;  $T_2^{\max}$ , the temperature of the maximum rate of this reaction; and  $m_2$ , the mass decrement in this reaction.

IR and UV-Vis spectra of films before and immediately after UV irradiation were recorded with Carl Zeiss (Jena) spectrophotometers. From the IR spectra the ratio of the absorbance of the carbonyl ( $A_{1733}$ ) band to the absorbance of the standard deformation band of the  $\text{CH}_2$  group ( $A_{1435}$ ) was calculated. The change in absorbance of these bands after irradiation was determined. From the UV-Vis spectra, the increase in absorbance coefficient after irradiation was determined for selected peaks:

$$\Delta a = \frac{A_t - A_0}{d} (m^{-1})$$

where  $A_0$  is the absorbance of the nonirradiated sample,  $A_t$  is the absorbance of this sample after irradiation time,  $t$  and  $d$  is the thickness of the sample ( $m$ ).

### Results and discussion

The small amount of PS in PVC films did not clearly affect their thermal stability. Temperature  $T_1^0$  did not change. The values of parameters  $T_2^0$ ,  $T_2^{\max}$  and  $m_2$  in the

**Table 1** Thermal parameters characterizing PVC films containing PS

Amount of PS in PVC, wt, %	$T_1^0$ , °C	$T_1^{\max}$ , °C	$m_1$ , %	$T_2^0$ , °C	$T_2^{\max}$ , °C	$m_2$ , %	$E_1$ , kJ/mol	$E_2$ , kJ/mol
0	200	250	60	360	430	17	187	271
1	195	275	56	370	435	20	162	245
2	200	280	54	370	435	19	147	223
3	200	265	57	370	435	19	139	208
5	200	260	56	370	435	20	120	200

presence of PS were only slightly larger (Table 1). At the same time, the distinctly decreasing activation energy [20] of dehydrochlorination,  $E_1$ , and of total decomposition of the PVC,  $E_2$ , with increase of the PS content in the films points out to the large, and possibly even dominant influence of the different conditions of decomposition on its course. These differences result from the different compositions of the films and thus from their different structures. It affects the diffusion rate or evaporation of gaseous products formed during decomposition.

After UV irradiation, the thermal stability of the studied samples was changed (Table 2). The dehydrochlorination temperature  $T_1^0$  decreased by 5 to 25 degrees. The decomposition temperature  $T_2^0$  similarly increased. The cause of the decrease of  $T_1^0$  was probably photodehydrochlorination initiated by the irradiation. This is confirmed by the smaller values of parameters  $m_1$ , caused by the partial release of HCl during irradiation. The reasons for the increase of  $T_2^0$  were probably photocrosslinking and photooxidation. The products of these processes require additional energy for their decomposition. The changes caused in  $T_1^0$  and  $T_2^0$  by the UV irradiation in samples of pure PVC are higher than those in samples containing PS, and decrease with increase of the PS content. This suggested that PS decreases

**Table 2** Changes of thermal parameters, increase of  $-(C=C)_n-$  and  $C=O$  groups and concentration and efficiency of crosslinking after UV irradiation of samples for 8 h

Amount of PS in PVC, wt. %	$T_1^0$ , °C	$T_2^0$ , °C	$m_1$ , %	Changes of $\Delta a \cdot 10^{-4} (m^{-1})$					$\frac{A_{1733}}{A_{1435}} 10^{-2}$	Gel content, wt. %
				312 <i>n</i> =4	328 <i>n</i> =5	368 <i>n</i> =7	394 <i>n</i> =8	491 <i>n</i> =9		
0	25	20	3	5.5	4.0	2.4	1.8	1.4	16.5	48
1	18	15	2	2.5	2.3	1.2	0.9	0.5	12.8	43
2	15	13	1	1.3	1.8	0.9	0.5	0.3	11.2	36
3	10	10	1	1.5	1.5	0.7	0.4	0.2	10.0	32
5	5	5	0.5	1.4	1.2	0.5	0.2	0.1	9.7	28

the efficiency of those photochemical processes in PVC which determined its  $T_1^0$  and  $T_2^0$  values, and that these changes are detectable by thermal analysis.

This was confirmed by the results of IR and UV-Vis analysis, which point to a smaller concentration of C=O groups (formed as a result of photooxidative processes) in samples containing PS (Table 2). Similarly, a smaller concentration of polyene groups (formed as a result of photodehydrochlorination) was observed in these samples. This relates to the wavelengths of 312, 328, 368, 394 and 491 nm to which the polyene structures  $-(C=C)_n-$  with  $n$  values of 4, 5, 7, 8 and 9, respectively, are attributed. Similarly, in samples containing PS the efficiency of the crosslinking process decreases with increase of the PS content in the PVC (Table 2).

As the Figures show, the smaller the efficiency of photodehydrochlorination (Fig. 1), photooxidation and crosslinking (Fig. 2), the smaller the changes in the temperature  $T_1^0$  and  $T_2^0$ .

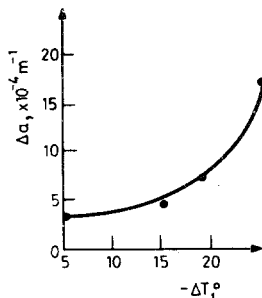


Fig. 1 Change of  $T_1^0$  depending on concentration of polyene group:

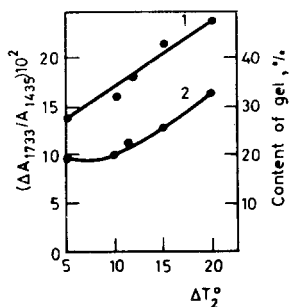


Fig. 2 Change of  $T_2^0$  depending on concentration of carbonyl group (1) and efficiency of crosslinking (2)

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**Zusammenfassung** — Der Einfluß der durch UV-Bestrahlung bei 253,7 nm hervorgerufenen fotochemischen Prozesse auf die thermische Stabilität von PVC wurde untersucht. Mittels der thermischen Untersuchungen wurde gefunden, daß im Ergebnis der im PVC stattfindenden fotochemischen Prozesse kleine Unterschiede bestehen. Fotodehydrochlorierung vermindert die Temperatur für die thermische Dehydrochlorierung, während Fotooxidation und Vernetzung die Temperatur für die vollständige Zersetzung dieses Polymers erhöhen.

**Резюме** — Изучена термоустойчивость поливинилхлорида (ПВХ) в зависимости от фотохимических процессов, происходящих в нем при облучении УФ светом с длиной волны 253,7 нм. Найдено, что небольшие различия в степени эффективности фотохимических процессов, происходящих в ПВХ, могут быть установлены термическими измерениями. При этом установлено, что фотодегидрохлорирование понижает температуру термического дегидрохлорирования, тогда как фотоокисление и образование поперечных связей повышает температуру полного разложения полимера.