

THERMAL AND PHOTOCHEMICAL STABILITY OF POLYSTYRENE AND ITS BLENDS WITH POLYVINYL CHLORIDE

II Photochemical transformation in polystyrene blends with polyvinyl chloride, and their thermal stability

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The influence of some irregularities in polystyrene (PS) and polyvinyl chloride (PVC) chains on their thermal stability was investigated. UV irradiation caused an increase in the content of these irregularities in the polymers. It was found that the presence of carbonyl groups and crosslinking of the polymer chains hamper the thermal dehydrochlorination of PVC and the total decomposition of both polymers. On the other hand, weak peroxy linkages (which facilitate degradation processes) and conjugated double bonds decrease the temperature of total decomposition of PS and PVC blends.

The results of our previous investigations indicated the stabilizing effect of polyvinyl chloride (PVC) on polystyrene (PS) and also that of PS on PVC during the thermal decomposition of blends containing 1, 2, 5, 10 or 20% of PVC in PS.

We suggested that PS hinders the dehydrochlorination of PVC because of the reaction of Cl· radical with the hydrogen on the tertiary carbon atoms of PS and not with its own hydrogen. This in turn facilitates the process of crosslinking of macroradicals. Both these processes may cause increases in the thermal parameters T_1 and T_2 [1].

In order to verify this assumption, the investigated samples were exposed to UV irradiation, causing photocrosslinking [2–8] and photodehydrochlorination [9–14] to occur in them. These processes should take place with different efficiencies in samples of different compositions. By subjecting them to thermal decomposition, we hoped to obtain evidence of the effects of the above processes and their efficiencies on the thermal stabilities of the samples. Besides the above photoprocesses, however, photodegradation [15–19] and photooxidation [20–37] may occur in both polymers (PS and PVC). The former process leads to a decrease in the limiting viscosity number (LVN), while the latter results in the formation of

hydroperoxide or peroxide groups, which very quickly undergo decomposition with the formation of hydroxy and carbonyl groups in the polymer chains, often with their degradation [2, 3, 37]. Finally, additional changes occur in the polymer chains. Attention is paid to the influence of these changes on the thermal stabilities of PS and PVC blends:

Experimental

Samples of PS with $\bar{M}_v = 360,000$ and its blends with 1, 2, 5, 10 and 20 wt% of PVC with $\bar{M}_v = 43,000$ were prepared in the form of films about 0.015 mm thick [1].

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.

IR and UV-Vis spectra of these 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 band (A_{1720}) to that of the standard deformation band of the CH_2 group (A_{2920}) was calculated. The change in absorbance of these bands after irradiation was determined.

From the UV-Vis spectra, the increase in absorbance coefficient (a) after irradiation was determined for selected peaks:

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

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

The gel fraction, formed in samples as a result of the crosslinking of the polymer induced by UV irradiation, was determined by extraction of the samples in cyclohexanone for 24 h. After the removal of insoluble gel from soluble sol, the gel was washed with methanol and dried, and its weight fraction was determined.

The LVN of the sol was determined at $25 \pm 0.05^\circ$ with the Ubbelohde viscometer.

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

Results and discussion

The temperature of thermal dehydrochlorination of PVC in PS films increased after its UV irradiation (Tables 1 and 2). In contrast, for pure PVC films irradiated under identical condition, a decrease of this temperature was observed [38]. This was explained by initiation of the dehydrochlorination process by UV irradiation and consequently the easier occurrence of this process under the influence of temperature. The opposite results were obtained in the presence of PS. This may be caused by the greater efficiency of the photooxidation and photocrosslinking processes which occur in PVC together with its photodehydrochlorination during irradiation of the samples. The products of these processes may retard the thermal dehydrochlorination, which occurs as a chain reaction, and as a consequence the thermal dehydrochlorination of PVC occurs at higher temperature. This effect is the more marked, the greater the content of PVC in the samples (Table 2).

Table 1 Thermal parameters characterizing irradiated samples of unmixed polystyrene and its blends with polyvinyl chloride

Amount of PVC in PS, wt. %	Thermal parameters							
	T_1^0 , °C	T_1^{\max} , °C	m_1 , mg	T_2^0 , °C	T_2^{\max} , °C	m_2 , mg	E_1 , kJ/mol	E_2 , kJ/mol
0	—	—	—	335	408	57	—	109
1	—	—	—	340	408	51	—	75
2	—	—	—	345	405	56	—	76
5	265	290	2	350	412	50	76	98
10	260	290	3	350	409	46	74	85
20	255	285	6	355	408	41	73	74

Table 2 Changes in thermal parameters on UV irradiation of polystyrene and its blends with polyvinyl chloride

Amount of PVC in PS, wt. %	Changes in thermal parameters							
	ΔT_1^0 , °C	ΔT_1^{\max} , °C	Δm_1 , mg	ΔT_2^0 , °C	ΔT_2^{\max} , °C	Δm_2 , mg	ΔE_1 , kJ/mol	ΔE_2 , kJ/mol
0	—	—	—	15	-7	-9	—	8
1	—	—	—	-28	-4	-10	—	10
2	—	—	—	-23	-5	-4	—	9
5	13	5	-2	-20	-13	-9	57	-110
10	15	10	-4	-12	-6	-13	37	-51
20	25	15	-9	-5	-12	-6	32	-38

The activation energy [39] of the dehydrochlorination process (E_1) in UV-irradiated samples increased several-fold. This confirms our assumption that the photochemical processes (crosslinking and oxidation) make it more difficult for the dehydrochlorination to take place (Table 2).

The results of qualitative and quantitative analysis of the photochemical transformations in the samples, and the changes caused in the temperature of thermal dehydrochlorination by these transformations, are presented in Fig. 1.

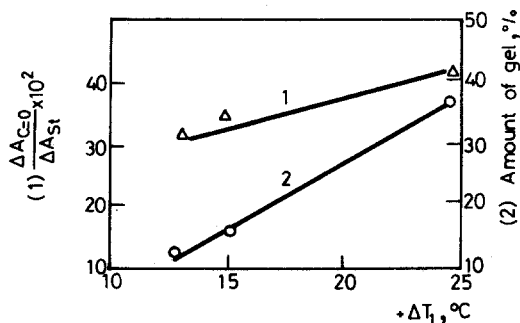


Fig. 1 Change in T_1^0 with concentration of C=O groups (1) and gel content (2)

The course of the curves in this Figure indicate that the greater the content of crosslinking and oxidation products in the samples, the greater is the increase in T_1 .

The temperature of complete decomposition of the irradiated samples, T_2 , and T_2^{\max} undergo a lowering; this lowering is the greater, the lower the content of PVC in the samples. At the same time, the insignificant but positive changes in these parameters for unmixed PS suggest that the lowering of T_2 and T_2^{\max} is initiated by the UV irradiation giving rise to weak chemical bonds, e.g. chain branching or/and peroxy linkage formation, which lead finally to degradation of the polymer chains. These processes occur with different efficiencies in samples with different compositions and their course is favoured by the better mixing of the two polymers.

A comparison of the photochemical transformations in the samples and the changes in their temperatures of complete decomposition (Fig. 2) demonstrates that photodegradation has the dominant influence on the decrease in thermal stability of the samples. The presence of the carbonyl group and crosslinking act in opposite directions on the value of parameter T_2 .

The activation energies of complete decomposition (E_2) for the irradiated samples reveal that the decomposition process requires less energy in the presence of PVC. Different factors, such as the composition of the blend, the fine structure of the polymer mixture, the diffusion of oxygen into the films, and the diffusion of degradation products, influence the value of the activation energy. Accordingly, irregularities were found to occur in the changes in E_2 .

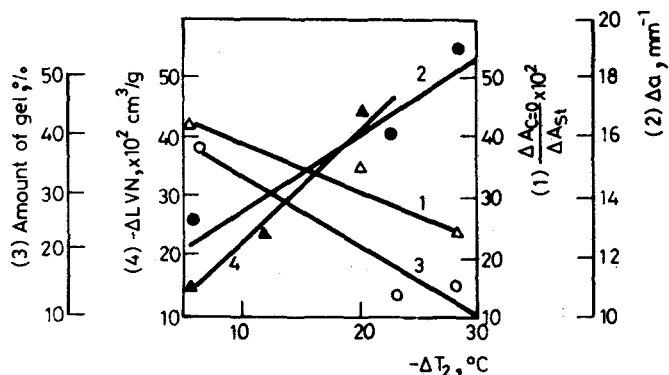


Fig. 2 Change in T_2^0 with concentration of C=O groups (1), polyene groups (2), gel content (3) and decrease in LVN (4)

For all samples, the changes in T_1 and T_2 are more significant than those in T_1^{max} and T_2^{max} (Table 2). This indicates that the beginning of the thermal processes is more sensitive than T^{max} to the composition of the blend, the structure of the polymer chains and the structure of the sample, depending on the miscibility of the two components. The lower values of m_1 and m_2 for the irradiated samples in comparison with this value for the nonirradiated samples, point to a partial loss in mass of the polymer as a consequence of its photolysis (Table 2).

The order of reaction of the thermal transformation has been found to be either 1 or 0, as was the case for the nonirradiated samples.

Conclusion

The above findings confirm our assumption [1] that the stabilizing effects of PVC on PS and of PS on PVC in blends of PS with 1–20% PVC result from the readily occurring crosslinking between the macroradicals of the two polymers. This process hampers the dehydrochlorination of PVC. The results also demonstrate that oxidation with the formation of carbonyl groups in the PVC chains acts against dehydrochlorination and thereby increases the thermal stability of both polymers. Processes causing a decrease in LVN lead to a decrease in thermal stability of blends of PS with PVC.

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Zusammenfassung — Es wurde der Einfluß von Unregelmäßigkeiten in Polystyrol (PS)- und Polyvinylchlorid (PVC)-Ketten auf deren thermische Stabilität untersucht. UV-Bestrahlung verursacht ein Ansteigen des Gehaltes an Unregelmäßigkeiten in den Polymeren. Es wurde festgestellt, daß die Gegenwart von Carbonylgruppen und Querverbindungen der Polymerketten die thermische Dehydrochlorierung von PVC und eine vollständige Zersetzung beider Polymere verhindern. Andererseits senken Peroxidverknüpfungen (die die Degradierungsvorgänge erleichtern) und konjugierte Doppelbindungen die Temperatur für eine vollständige Zersetzung von PS und PVC Gemischen.

Резюме — Изучено влияние некоторых нарушений в цепях полистирола и поливинилхлорида на их термоустойчивость. УФ-облучение вызывает некоторое увеличение содержания таких нарушений. Найдено, что наличие карбонильных групп и сшивания полимерных цепей затрудняет термическое дегидрохлорирование ПВХ и общее разложение обоих полимеров. Наличие же слабых перекисных звеньев, способствующих процессу разложения, а также сопряженных двойных связей, приводит к уменьшению температуры общего разложения смесей полистирола и поливинилхлорида.