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

Influence of small amount of PVC in PS films on their thermal parameters

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The influence of a 1–20% content of PVC in PS films on their thermal stability was investigated. It was found that the thermal stabilities of these blends are higher than that of either of the two pure polymers. This indicated the mutual stabilizing effects of these polymers on each other. The effect is significant when the PVC content in the blends is 1–5%.

A higher amount of PVC causes either no significant change or a lowering of the thermal stability. The miscibility of the polymer components in the blends clearly has an important influence on the course of the thermal processes.

Polystyrene (PS) is an excellent polymer for various uses. Its properties can be modified by different means, for example chemically through copolymerization or physically by blending with different materials. At present, physical modification by blending with other polymers is rapidly assuming an important role.

PS has only a fair stability for most uses, as it has a rather low heat resistance [1, 2]. Again, polyvinyl chloride (PVC), another industrially important polymer, is quite susceptible towards heat and its instability has stimulated many workers to investigate this polymer [3–5].

As blends or as graft copolymers, both these polymers have a higher thermal stability than that of PS or PVC alone [6–8].

The aim of our work was investigate the influence of small amounts of PVC in films of PS on the thermal stability when the polymers show fairly good mixing, and variation in this influence with variation in the degree of miscibility.

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Experimental

The samples of PS and its blends with 1–20 wt.% of PVC were prepared in the form of films about 0.015 mm thick. They were obtained by solvent evaporation from 2% benzene and 2% benzene+cyclohexanone solution, respectively. The solution of the polymers was poured on to horizontal glass plates and the solvent was allowed to evaporate at 22°, leaving the polymer in the film form on the glass plates. The films were dried and then extracted in methanol at room temperature to remove cyclohexanone; this was controlled by IR analysis.

The intrinsic viscosities of PS and PVC were found to be 120 $\mathrm{cm^3/g}$ and 80.5 $\mathrm{cm^3/g}$ at 25° in benzene and cyclohexanone as solvent, respectively.

Thermal analyses were carried out in a Paulik–Paulik–Erdey OD 102 derivatograph in nitrogen atmosphere and at a heating rate of 5 deg/min up to 500°; the sensitivity for TG was 100 mg.

A single-stage process of thermal decomposition of PS and a two-stage one for the blends PS + PVC were revealed by one and two peaks, respectively in DTG. The following characteristic parameters of the peaks were defined:

T_1 = temperature of onset of reaction 1 (dehydrochlorination of PVC);
$T_1^{\max}$ = temperature of maximum rate of reaction 1;
T_2 = temperature of onset of reaction 2 (total decomposition of polymers);
$T_2^{\max}$ = temperature of maximum rate of reaction 2.

The two-stage mass loss in the TG curve allows determination of:

Δm_1 = mass decrement in process 1,
Δm_2 = mass decrement in process 2.

Results and discussion

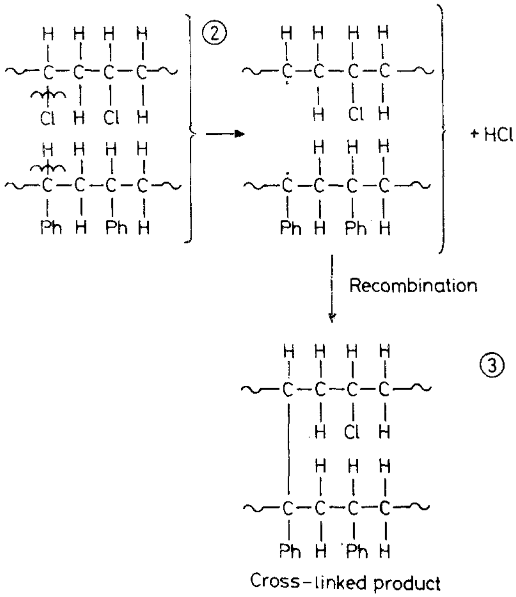
In Fig. 1 the change in the dehydrochlorination temperature of PVC are plotted versus its amount in PS.

The dehydrochlorination peak in the DTG curve was clearly seen when the PVC content was 5% or more. When the content of PVC was smaller, this peak was absent.

The values of T_1 and $T_1^{\max}$ for all the blends studied are higher than those for pure PVC, which were found to be 195° and 254°, respectively, under the same condition [9].

This indicates that PS has a stabilizing action on the dehydrochlorination of PVC, which takes place as a chain reaction according to Scheme 1 [10].

$$\left.\begin{array}{l} -CH_2-CHCl- \longrightarrow -CH_2-\dot{C}H- + Cl\cdot \\ Cl\cdot + -CH_2-\dot{C}H- \longrightarrow -CH=CH- + HCl \\ Cl\cdot + -CH=CH-CH_2-CHCl- \longrightarrow -CH=CH-\dot{C}H-CHCl- + HCl \\ -CH=CH-\dot{C}H-CHCl \longrightarrow -CH=CH-CH=CH - + Cl\cdot \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{etc.} \end{array}\right\}$$ ①



This action can be attributed to the reaction of splitting-off of a Cl radical with a tertiary hydrogen atom from PS (2). As a consequence, the chain reaction of dehydrochlorination stops and requires renewed initiation, as revealed by the retarding of this reaction and its subsequent course at a higher temperature. The linear decreases in T_1 and T_1^{max} with increase of the PVC content in PS is probably caused by the deterioration of the miscibility of these polymers with each other, observed via the increasing turbidity of the films with higher contents of added PVC; there is an increasing tendency to the formation of separate phases (Pictures 1–3), with a lower chance for reaction (2) to take place.

The temperatures of total decomposition T_2 and T_2^{max} of the polymers vs. the PVC content in the samples are presented in Fig. 2. These temperatures, and especially T_2, show a rapid rise, reaching a peak, and then a fall, though not so markedly. For both T_2 and T_2^{max}, this peak occurs at about 5% of PVC in the sample.

The rise in thermal stability of PS in the presence of PVC, and also that of PVC ($T_2 = 356°$, $T_2^{max} = 420°$) in the presence of PS, may be caused by the cross-linking process (3), facilitated by reaction (2), but the efficiency of this may fall as the

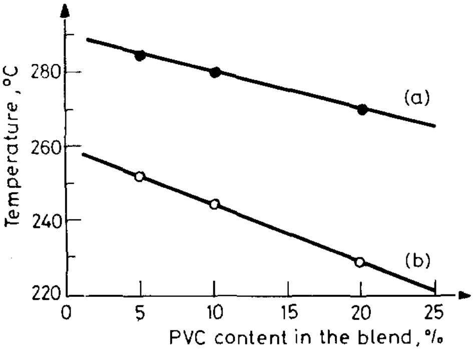


Fig. 1 T_1^{max} (a) and T_1 (b) of PS films containing different amounts of PVC

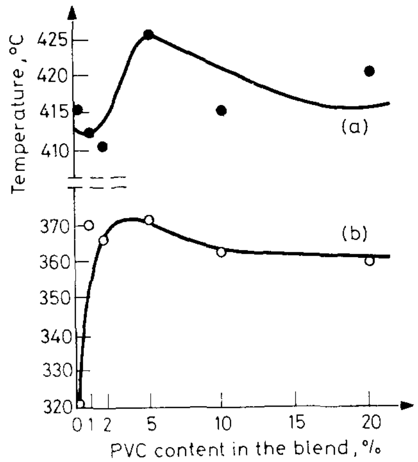


Fig. 2 T_2^{max} (a) and T_2 (b) of PS films containing different amount of PVC

miscibility of the components deteriorates. From this, we can explain the peaks of T_2 and T_2^{max} occurring at a PVC content of about 5%.

Also, the rise in thermal stability of the polymers may be caused by the presence of conjugated double bonds in them, produced as a result of reaction (1) [11]. Figure 3 is a plot of the change in mass of the sample during dehydrochlorination and during decomposition with increasing PVC content in the samples. The loss in mass at the end of the dehydrochlorination stage increases with increase of the PVC content in the samples and follow a linear path through the origin (Fig. 3, curve *a*). An increase in loss in mass during dehydrochlorination is expected, as a higher amount of PVC in the blend would give off a proportionally larger amount of hydrogen chloride during dehydrochlorination.

The loss in mass at the end of the decomposition stage (Fig. 3, curve *b*) shows a decrease with increase of PVC content, again following a linear pattern. The fall in the loss of mass at the end of the second stage indicates the formation of ever larger amounts of thermally stable solid during degradation. This suggests that, during the thermal processes, more and more cross-linked products and conjugated double bonds from PVC are formed as the amount of PVC in the blend increases.

This is confirmed by observation of the change in sample mass during heating (Table 1). During the process of dehydrochlorination in the temperature range

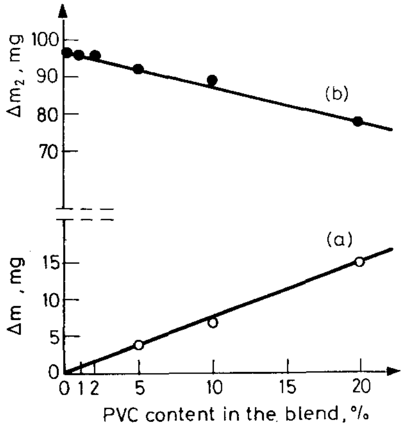


Fig. 3 Dependence of mass decrement Δm_1 (a) and Δm_2 (b) on the amount of PVC in PS films

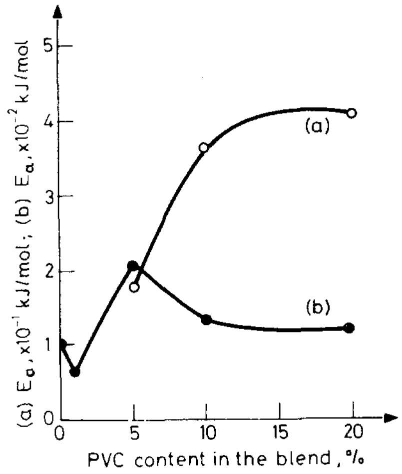
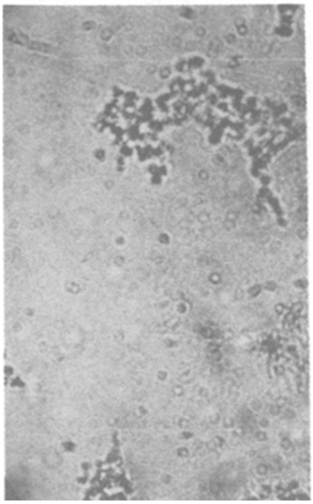


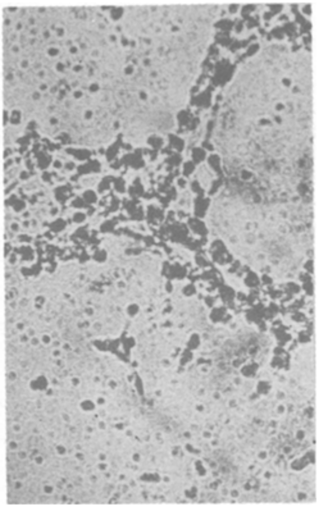
Fig. 4 Plot of activation energy of dehydrochlorination $E_a \cdot 10^{-1}$ (a) and decomposition $E_a \cdot 10^{-2}$ (b) *vs.* PVC content in PS films

Table 1 Change in sample mass during heating

Content of PVC in PS, wt%	Residue, wt%, at temperature, °C							
	250	300	350	370	390	400	420	440
0	99	99	95	92	81	60	20	2
1	99	98	97	96	91	80	16	2
5	99	96	95	94	93	90	51	6
10	99	93	91	90	85	70	20	4
20	99	89	85	84	81	76	41	12



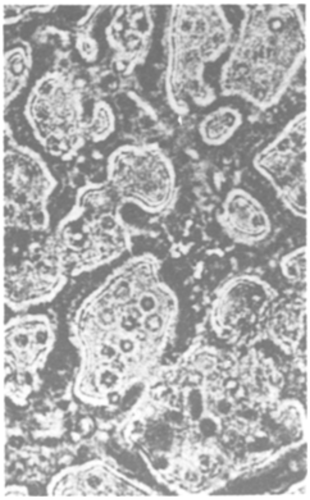
Picture 1 Structure of PS films containing 2% of PVC. Total magnification 1400 ×



Picture 2 Structure of PS film containing 5% of PVC. Total magnification 1400 ×

250–390°, the residue from samples containing PVC decreases with increasing PVC content. On the other hand, during the processes of complete decomposition 400–450°, the residue from the samples containing PVC is greater than that from samples of pure PS. The data suggest that the efficiency of formation of highly thermally stable structure is the highest in the presence of 5% of PVC in the blend.

To study the kinetics of the process, the activation energies of thermal decomposition of PS and its various blends with PVC were calculated by the method of Coats and Redfern [12]. The process of thermal decomposition was followed dynamically from room temperature up to 500°. Inspection of the thermal curves reveals that the dehydrochlorination stage becomes readily discernible from a composition containing of 5% PVC. A dynamic method of thermal analysis is more complex by virtue of the fact that, during a non-isothermal decomposition, many consecutive parallel or overlapping reactions take place, and the calculated activation energy is therefore only an assessment of the summation of the activation energies of all these processes. However, as the dehydrochlorination stage is clearly visible in the thermal curve, the activation energies of dehydrochlorination and of thermal decomposition were calculated separately and plotted. The Coats–Redfern method assumes that the order of reaction should be one of 0, 1/2, 2/3 or 1, as in solid-state reactions it is theoretically justified to assume only such reaction orders [13]. A computer program was written for this purpose and the best straight lines from all the possible orders of reaction (0, 1/2, 2/3 and 1 in this case) were found via the criterion of the regression coefficient. The calculated order of reaction, n, remained at 1 during the dehydrochlorination stage for all blends in the temperature range 205–371°. During complete decomposition, it is 1 for 20% and 5% PVC contents in the blends, and 2/3 for a 10% PVC content, while it is 0 for samples containing 1% PVC and for pure PS in the temperature range 205–460°.



Picture 3 Structure of PS film containing 10% of PVC. Total magnification 1400×

The activation energy for dehydrochlorination can be seen (Fig. 4) to rise from 18.49 kJ/mol at 5% PVC to 36.8 kJ/mol for 10% PVC before levelling off at 41.48 kJ/mol for 20% PVC in the samples. This does not agree well with our T_1 and T_1^{max} data in Fig. 1, which point to a steady decrease of T_1 and T_1^{max} with rising PVC content. Though there is a fall in T_1 and T_1^{max}, the rise in the activation energy of dehydrochlorination can be seen as due not only to the elimination reaction of HCl, but also to one controlled by the diffusion of volatiles from the films. This diffusion is again governed by the morphological structure of the film, provided other factors remain constant.

On the other hand, the activation energy of decomposition rises from a value of 101.7 kJ/mol for pure PS, up to 207.8 kJ/mol at 5% PVC content, and then again falls off to a value of about 111.9 kJ/mol for samples with 20% PVC; this is nearly the same value as for pure PS. Such a trend agrees quite well with the T_2^{max} data in Fig. 2.

This confirmed once again that the structure of the polyblend films has a great influence on the course of the thermal degradation processes.

Conclusion

In the presence of PVC, films of PS show a higher thermal stability. The stabilizing influence of PVC on PS, and also of PS on PVC is significant when the PVC content in the films is 1–5%.

A higher amount of PVC in PS causes either no significant change or a lowering of the stability. This indicates that the degree of mixing of the polymers, and consequently the structure of the films, decides the course of the thermal processes of degradation and the thermal stability of polyblend films.

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Zusammenfassung - Der Einfluß von 1–20% PVC in PS-Filmen auf deren thermische Stabilität wurde untersucht. Es wurde festgestellt, daß die thermische Stabilität dieser Gemische höher ist, als die der beiden reinen Polymere für sich. Dies verdeutlicht den gegenseitigen Stabilisierungseffekt der beiden Polymere. Zu einem signifikanten Effekt kommt es bei einem PVC Gehalt der Gemische von 1–5%. Ein höherer Gehalt an PVC führt entweder zu keiner signifikanten Veränderung oder zu einer Abnahme der thermischen Stabilität. Die Mischbarkeit der Polymerkomponenten des Gemisches verfügt eindeutig über einen wichtigen Einfluß auf den Ablauf der thermischen Prozesse.

Резюме — Изучена термоустойчивость полистирольных пленок в зависимости от содержания в них поливинилхлорида (ПВХ) от 1 до 20%. Найдено, что термоустойчивость таких смесей более высокая по сравнению с чистыми исходными полимерами, что свидетельствует о взаимном стабилизирующем эффекте полимеров друг на друга. Значительное стабилизирующее действие наблюдается при содержании ПВХ равным 1–5%. Более высокое процентное содержание ПВХ или не вызывает увеличения термоустойчивости или же вызывает даже ее понижение. Смешиваемость полимерных компонент в смесях оказывает значительное влияние на ход термических процессов.