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THERMAL STABILITY OF POLYSTYRENE BLENDS WITH POLYBUTADIENE, AND EFFECTS OF MISCIBILITY OF THE TWO POLYMERS ON THERMAL PARAMETER VALUES

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The influence of a 1-20% content of polybutadiene (PB) in polystyrene (PS) films on their thermal stability was investigated. It was found that the thermal stabilities of these blends are higher than that of pure PS. This stabilizing effect is significant when the PB content in the blends is 1%. A higher amount of PB causes either no significant change in the thermal stability of the blends (determined in nitrogen) or a rise in thermal stability (determined in air). The cause of these changes is the crosslinking and oxidation which occur with varying efficiency, depending upon the miscibility of the two polymers.

Polystyrene (PS) is a widely known polymer which has found applications in many fields. It is a very important commercial material with many desirable properties. It is a clear, transparent thermoplastic material which softens at about 100°. It is resistant to acids, alkalis and alcohols. PS has very good dimensional stability and is highly resistant to water. It is used for mouldings, coatings and sheet. PS is known for its excellent electrical insulation properties. The high level of optical clarity and high refractive index make it a very important material for optical devices where surface abrasion is not a problem. Though the above properties make PS a very attractive polymer for many uses, its outdoor applications are severely restricted as it loses its properties and becomes yellow and brittle on long outdoor exposure or exposure to heat or to UV radiation [1-20]. The thermal and photochemical stabilities of PS may be changed by the addition of stabilizing substances [21-22].

The aim of our work was to investigate the influence of small amounts of polybutadiene (PB) in films of PS, and also the miscibility of the two polymers, on their thermal stability, and to identify the thermal processes occurring in these polymers before their complete decomposition.

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Experimental

The samples of PS and its blends with 1-20 wt.% of PB were prepared in the form of films about 0.015 mm thick. They were obtained by solvent evaporation from 2% benzene solution. The solution of the polymers was poured onto 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 and again dried under reduced pressure to constant weight.

Thermal analyses were carried out in a Paulik-Paulik-Erdey OD 102 derivatograph in nitrogen and air atmospheres, at a heating rate of 5 deg/min, up to 500°. The following characteristic of the peaks in DTG and TG were defined:

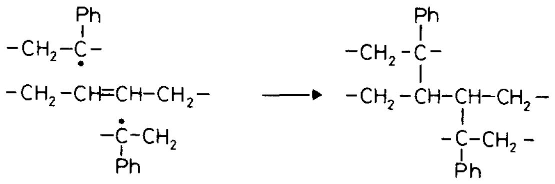
T^{o} = onset temperature of complete decomposition of polymers;
T^{max} = temperature of maximum rate of decomposition;
Δm = mass loss in decomposition process.

IR spectra of pure PS films and films containing different amount of PB, before and after heating for 2 h at 200° in air or nitrogen, were recorded with a Carl Zeiss UR 10 spectrophotometer (Jena). In these samples, the gel fraction formed as a result of thermal crosslinking was determined by extraction of the samples in benzene 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.

Results and discussion

A small amount (1 %) of PB in PS films increased the thermal stability of the PS. The temperature of total decomposition (T^{o}) increased by about 25°. A higher content of PB in the blends did not influence T^{o} markedly (Table 1). The addition of PB to PS did not clearly affect the values of the parameters T^{max} and Δm. However, the activation energy of the decomposition process increased similarly to T^{o}, especially for blends containing 1-3% of PB.

The reason for the increase in thermal stability of PS is probably the easier formation of crosslinks in the reaction of PB dimacroradicals with macroradicals of PS, than between PS macroradicals alone:



or the quenching of the macroradicals formed with PS by PB macromolecules:

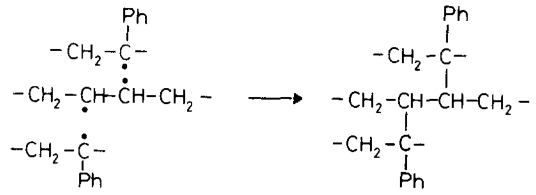


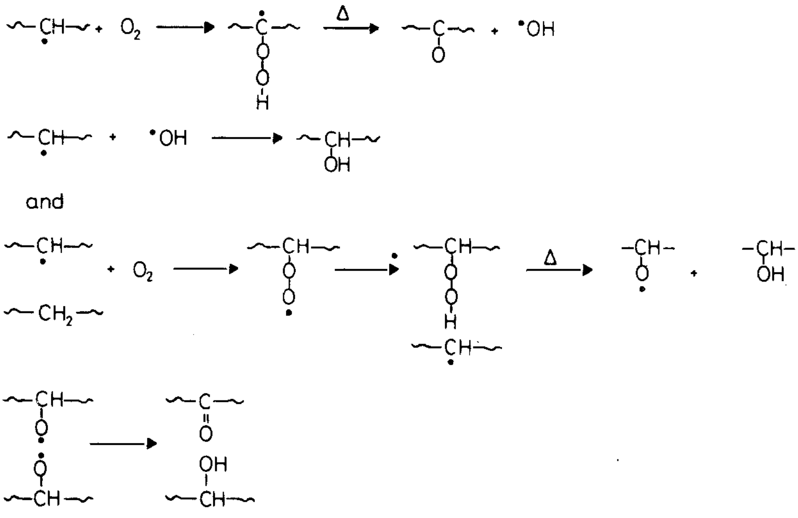
Table 1 Characterization of the thermal transformation in PS and its blends with PB (nitrogen atmosphere)

Content of PB in PS films, %	Thermal parameters				Gel content, %
	T^o, °C	T^{max}, °C	Δm, %	E, kJ/mol	
0	335	432	99	261	7.6
1	360	435	100	300	11.0
3	363	440	100	309	8.1
6	360	435	100	294	8.5
10	366	438	100	267	8.0
20	368	440	99	273	7.9

These reactions may occur only on contact of the macromolecules and macroradicals of the two polymers. This is possible only in the event of the good miscibility of the two components, i.e. at a low content of the second polymer. The results (Table 1) suggest that this occurs at 1% of PB in the blends. It is confirmed by the higher content of gel formed as a result of thermal crosslinking. The merely slight changes in T^o and E in the blends containing 10 and 20% of PB point to the lack of increase in the contacts between the two polymers and to the deterioration of their miscibility.

A greater increase in the thermal stability of PS in the presence of PB was found during the decomposition of these blends in air atmosphere. The maximum increase in T^o, T^{max} and E was 50°, 40° and 90 kJ/mol, respectively (Table 1).

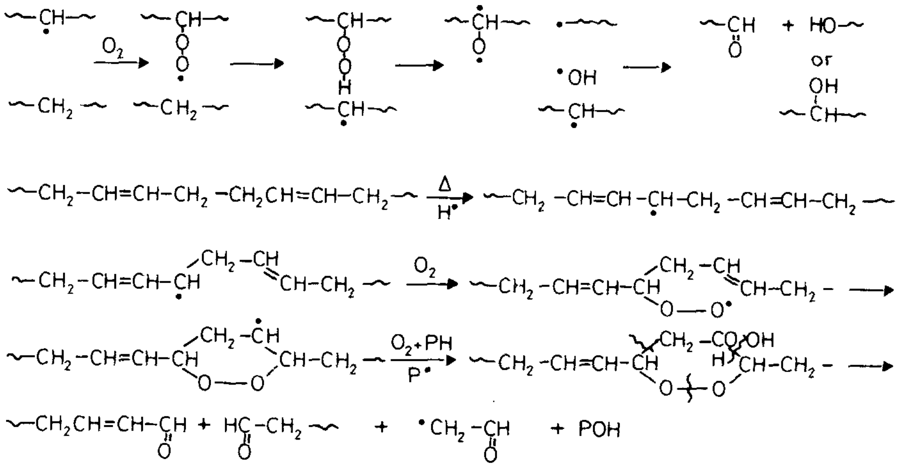
The increases in these parameters with increase of the PB concentration in the blends suggest that the reactions mostly occur in the PB independently of the miscibility of the two polymers. These reactions probably involve thermal oxidation. In these reactions, two macroradicals may react with oxygen to form macromolecules with C = O and OH groups:



The concentration of these groups increases with increase of the PB content int he blends (Table 2). This points to the greater susceptibility of PB to thermal oxidation in comparison with PS. It is confirmed by the decreasing values of Δm, which indicates an increasing content of heavier products of oxidation.

The results of IR analyses demonstrating the changes in the concentration of C = O and OH groups in the blends reveal that even a small amount of PB in PS retards these oxidation processes.

Some of the oxidation processes may involve breaking of the links in the main chains (oxidative degradation). The mechanism of these reactions for the two polymers is as follows:



These reactions cause apparent decreases in the decomposition temperature and the activation energy of decomposition in air, in contrast with the values of these parameters in nitrogen.

Table 2 Characterization of the thermal transformation in PS and its blends with PB (air atmosphere)

Content of PB in PS films, %	Thermal parameters				Oxidation product	
	T^0, °C	T^{max}, °C	Δm, %	E, kJ/mol	C=O	OH
0	251	390	99	136	0.05	0.02
1	259	400	98	170	0.03	0.01
3	260	370	97	166	0.07	0.01
6	280	380	94	190	0.13	0.03
10	300	425	95	225	0.17	0.06
20	290	438	93	141	0.28	0.09

The greatest changes in T^0 and E were found in the samples containing 1 and 3% of PB (Table 3). This may suggest that the oxidative degradation occurs with the greatest efficiency in these samples, and that the good miscibility of the polymers permits this degradation. It may also suggest that this process occurs more easily between two different PS and PB macroradicals than between identical ones.

Table 3 Differences between values of thermal parameters determined in nitrogen and air atmospheres

Content of PB in PS films, %	$-\Delta T^{o}$, °C	$-\Delta T^{max}$, °C	$-\Delta E$, kJ/mol
0	77	35	109
1	101	28	130
3	103	64	146
6	80	61	104
10	66	13	29
20	78	2	132

Conclusion

A 1% content of PB in PS increases the thermal stability of the PS and retards its thermal oxidation to yield C=O and OH groups. A greater amount of PB in the blends, has a less distinct or even the reverse effect. This is evidence of the decisive influence of the miscibility of the two polymers on the course and efficiency of the thermal processes in these blends.

References

1 O. Kysel, Chem. Zvesti, 19 (1965) 490.
2 J. Boon and G. Challa, Macromol. Chem., 84 (1965) 25.
3 H. H. G. Jellinek, J. Polym. Sci., 3 (1948) 850 and 4 (1949) 14.
4 S. L. Madorsky, J. Polym. Sci., 9 (1952) 133.
5 G. G. Cameron and G. P. Kerr, Europ. Polym. J., 6 (1970) 423.
6 B. V. Kokta, J. L. Valade and W. N. Martin, J. Appl. Polym. Sci., 17 (1973) 1.
7 A. Nakajima, F. Hamada and T. Shimizu, Makromol. Chem., 90 (1966) 229.
8 O. Chinatore, L. Costa and N. Grassie, Polym. Degrad. Stab. 3 (1981) 202.
9 T. Kuroki, T. Ikemura, T. Ogawa and Y. Sekiguchi, Polymer, 23 (1982) 109.
10 V. N. Esenin, I. A. Krasotkina and G. E. Zaikow, Vysokomol. Soedin., B, 25 (1983) 48.
11 I. Shopow and Ch. Iossopov, Makromol. Chem., 183 (1982) 2957.
12 L. A. Matheson and R. F. Boyer, Ind. Eng. Chem., 44 (1952) 867.
13 M. J. Reiney, M. Tryon and B. G. Achhammer, J. Res. Natt. Bur. Stand., 51 (1953) 155.
14 A. Kaminska, Polimery, 15 (1970) 338, 17 (1972) 195 and 365.
15 H. C. Beachel and L. H. Smiley, J. Polym. Sci., A 1, 5 (1967) 1635.
16 N. Grassie and N. A. Weir, J. Appl. Polym. Sci., 9 (1965) 975, 987, 999.
17 J. F. Rabek and B. Ranby, J. Polym. Sci., A 1, 12 (1974) 273, 295.
18 L. Dulog and K. H. David, Makromol. Chem., 145 (1971) 67.
19 J. B. Lawrence and N. A. Weir, J. Polym. Sci., A 1, 11 (1973) 105.
20 H. H. Jellinek and S. N. Lipvac, Macromolecules, 3 (1970) 237.
21 A. Jamieson and I. C. McNeill, J. Polym. Sci., Chem. Ed., 14 (1976) 353, 603.
22 A. Kaminska, S. Sanyal and H. Kaczmarek, J. Thermal Anal., 35 (1989) 78.

Zusammenfassung — Es wurde dir thermische Stabilität von Polystyrolfilmen mit einem Polybutadiengehalt von 1-20% untersucht. Es konnte festgestellt werden, daß die thermische Stabilität dieser Mischungen höher liegt als die von reinem Polystyrol. Ein ausgeprägter Einfluß läßt sich bei einem Polybutadiengehalt der Gemische von 1% erkennen. Ein höherer Polybutadiengehalt führt entweder zu keiner weiteren nennenswerten Veränderung der thermischen Stabilität (in Stickstoff) oder zu einer höheren thermischen Stabilität (in Luft) der Gemische. Der Grund für diese Veränderungen liegt in Abhängigkeit von der Mischbarkeit beider Polymere in einer unterschiedlich starken Vernetzung bzw. Oxydation.