Thermochimica Acta, 93 (1985) 187-190
Elsevier Science Publishers B.V., Amsterdam

THERMAL DEGRADATION OF ABS

M.P. Luda di Cortemiglia, G. Camino, L. Costa, M. Guaita

Istituto di Chimica Macromolecolare dell'Università

V. G. Bidone, 36 - 10125 Torino, Italy

ABSTRACT

Thermal degradation of polymers and copolymers of acrylonitrile, styrene and butadiene heated separately or blended (ABS) is studied by means of thermogravimetry and thermal volatilization analysis.

INTRODUCTION

Polymer blends are of growing importance in the field of polymeric materials since they provide a relatively simple way to produce new materials with specific properties, which are in general combination of those of the single polymers. However, the thermal behaviour of polymer blends may be different from the one expected on the basis of the behaviour of the polymers heated separately. This has been show to be due, for example in the case of binary blends, to radicals propagating the degradation of one polymer, which in the blends can react with the second one.[1]

Although blends involving polymers and copolymers of acrylonitrile, styrene and butadiene (ABS) are finding ever increasing application, little has been published on their thermal degradation mechanism. The preliminary results we have obtained in a systematic study of the thermal degradation of ABS resins are reported and discussed here.

EXPERIMENTAL

Materials

ABS samples were industrial blends (Riveda, Italy) of 33% by weight of polybutadiene onto which a styrene-acrylonitile copolymer (SAN) is grafted (PBg) and 67% of the same SAN copolymer. Separate samples of PBg, of SAN and of the polybutadiene prior to the grafting reaction (PB) were also studied.

The SAN copolymer contains 75% by weight of styrene and 25% of acrylonitrile.

The composition of PB is 52% 1,4-trans-, 30% 1,4-cis-, 18% 1,2-structural

---

Proceedings of ICTA 85, Bratislava

units. The weight ratio PB/SAN in PBg is 2/3. Infrared analysis shows that grafting of SAN occurs preferentially onto the 1,4-cis- structural units of PB.

Techniques

The thermal degradation of ABS, SAN, PB and PBg was studied by using thermal volatilisation analysis (TVA) and thermogravimetry.

TVAs were carried out at 10°C/min heating rate on 20 mg samples under dinamic vacuum, and rate of evolution of products of degradation volatile at 25°C and at -196°C were continuosly monitored. Condensable gaseous products were analysed at the end of degradation by Fourier Transform infrared (FTIR) after collection in a gas cell. Products volatile at degradation temperature but condensed at room temperature in the water cooled section of the degradation vessel (cold ring fraction, CRF) were collected and analysed by FTIR on NaCl disc. Thermogravimetries were carried out on 10 mg samples at 10°C/min heating rate under nitrogen flow (60 cm^3/min)using a Du Pont thermobalance.

RESULTS AND DISCUSSION

Since ABS is a complex system, it is convenient to study at first the thermal degradation of the simpler macromolecular structures of which it is constituted, i.e. SAN and PB By comparing these results with those obtained from the thermal degradation of PBg, the effect of grafting the SAN chains onto PB will be shown. Finally, the thermal behaviour of PBg and SAN degraded separately could be compared with that of ABS to recognise interactions occurring on blending PBg with SAN.

TG and TVA curves concerning thermal degradation of SAN, PB, PBg and ABS are shown in figure 1(a-d).

The SAN copolymer shows a single volatilisation step with maximun rate at 425°C preceeded by the evolution of a minor amount of residual monomers at about 200°C (figure 1-a). The major volatile products are chain fragments, NH_3, HCN, aromatic compounds in agreement with previous results on the thermal degradation of styrene-acrylonitrile copolymers.[3]

The thermal degradation of PB takes place in two overlapping steps (figure 1-b) TVA curves and analysis of the degradation products show that in the first step, corrisponding to a total volatilisation <20% of the initial weight of the sample, chain fragments and condensable gaseous hydrocarbons are evolved. In the second step,corresponding to the major weight loss, also non condensable gases are evolved (H_2 and CH_4).

Two major effects, thermal destabilization and increase of amount of residue at 600°C, are induced by grafting SAN chains to PB. This is evidenced in figure 1-c, where the TG curve obtained by heating PBg is compared whit the one calculed as a linear combination of those in figures 1-a and 1-b.

The peaks in the TVA curve in figure 1-c with maximun volatilization rate at 450°C, and corresponding to the evolution of products non condensable at 25°C and at -196°C, closely correspond to the peaks in the TVA curve of PB in figure 1-b. Therefore it is reasonable to conclude that the thermal decomposition of polybutadiene structures in PBg is unaffected by grafting SAN onto PB. On the other hand, the peak in figure 1-c with a maximun volatilization rate at 400°C should arise from the decomposition of SAN chains which, however, by comparison with the TVA curve of figure 1-a is shown to occur at the temperature 25°C lower than the decomposition of pure SAN. It follows that the overall thermal destabilization induced by grafting SAN onto PB, referred to above, is likely to involve SAN structures.

This effect is not evident in the TG and TVA curves of ABS (figure 1-d) probably because the total amount of grafted SAN chains corresponds to only about 20% of the total weight of the sample. A more detailed study of the thermal degradation of ABS is in progress to see if interactions take place between SAN and PBg during degradation.

REFERENCES

1 I.C. Mc Neill, in "Developments in Polymer Degradation", vol.1, Applied Sciences Publishers, London 1977

2 I.C. Mc Neill, Eur. Polym. J., 6 (1970) 373

3 N. Grassie and D.R. Bain, J. Polym. Sci., A-1, 8 (1970) 2653, 2665, 2679

4 N. Grassie and A. Heaney, Eur. Polym. J., 10 (1974) 415

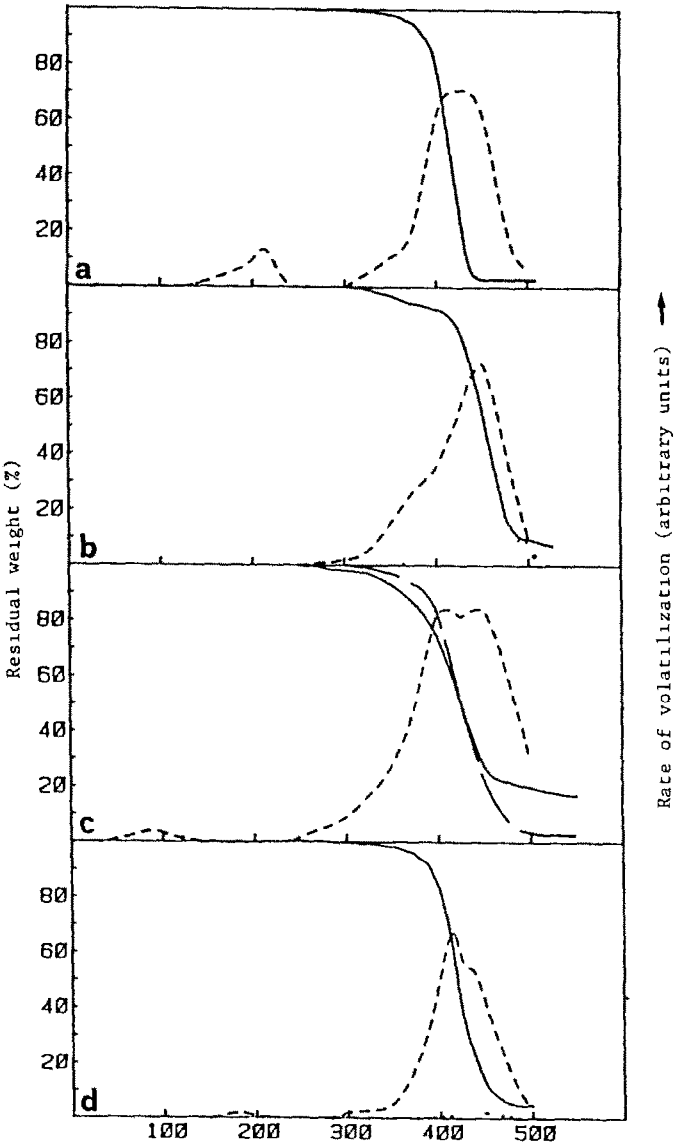

Fig 1· TG and TVA curves of SAN (a), PB (b), PBg (c) and ABS (d)
(———) TG curves; (—·—) calculated TG curve, (-----) TVA curves, 25°C trace, (······) TVA curves, −196°C trace