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TG AND DSC STUDIES OF SOME THERMAL PROPERTIES AND STABILITY ASPECTS OF POLY(ACRYLONITRILE BUTADIENE STYRENE), POLYSTYRENE AND POLY(ACRYLONITRILE STYRENE) PLASTICS

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ABSTRACT

The thermal-oxidative fumes of poly(acrylonitrile butadiene styrene) [9003-56-9], polystyrene [9003-53-6] and poly(acrylonitrile styrene) [9003-54-7] thermoplastics have been shown to have biochemical effects on rats and are therefore considered potentially toxic. The stability of these polymers with respect to temperature was studied. Their dynamic thermogravimetric curves, at 10 K/min, and differential scanning calorimetric curves, at 6 K/min, in air and nitrogen are presented. The temperatures of onset, peak and end of thermal degradation in the two atmospheres for each polymer were determined.

INTRODUCTION

Poly(acrylonitrile butadiene styrene) (ABS), polystyrene (PS) and poly(acrylonitrile styrene) (SAN) thermoplastics emit a variety of potentially toxic volatile compounds when subjected to elevated temperatures [1-3]. As part of on-going work in the assessment of the environmental and health risks posed by these plastics, the volatile compounds they emit during thermal decomposition are currently being studied and documented [4].* The temperatures of onset, peak and end of emission of volatiles during degradation are important to this kind of work. The thermal decomposition profiles of the above plastics were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). Apart from the need to provide independent data, the study was undertaken because the required thermal stability information on the particular samples being studied was not readily available.

TG and DSC critical parameters include heating rate, sample size and decomposition atmosphere [5,6]. Sample size and thickness tend to influence the decomposition mode and instrumental response through heat-transfer and mass transport effects [3,7-9]. Mertens has carried out a systematic investigation of the influence of operating

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parameters on the distribution of volatile compounds from decomposing PS and shown that part of the degradation always occurs before the steady state pyrolysis temperature is reached no matter what heating rate is used [10]. There thus exists some controversy regarding the exact decomposition temperature of plastics in general. On the whole, the occurrence of simultaneous heat and mass transfer problems depends on the experimental conditions and the chemical mechanism of the process under study. Plastic molecular weight has also been known to influence thermal decomposition temperatures [11-13]. Other pit falls of TG and DSC include susceptibility to sample container catalytic effects [14].

Variations of the temperatures of onset, peak and end of thermal degradation of plastics with heating rates have been well documented [15-18]. The temperature of onset of degradation has been shown to be less sensitive to changes in heating rate and has consequently been recommended for use in characterization of the thermal stability of plastics. For more stringent requirements a correction term which takes the dependence of thermal stability on the temperature interval between initial and final degradation temperatures into account can be added. The reciprocal of the rate constant for the initial degradation step has also been suggested as a viable characteristic quantity. The temperature at the end of degradation of some polymers has been found to be independent of the heating conditions, decomposition atmosphere and sample geometry [19]. It is therefore viewed as characterizing the total thermal instability of polymers. The time corresponding to loss of half of the initial weight in a given degradation is yet another characteristic of plastic thermal stability [20]. The objective of this study was to obtain representative average thermal decomposition temperatures of the plastics under study.

EXPERIMENTAL

The plastic samples studied in these experiments were: ABS 550 - 27, Dow Chem. GB (supplied by ALGOL OY of Finland); PS XP 5536, Dow Chemicals; and SAN LURAN 368 R BSF L.M.E.

The TG measurements were made with a Mettler TA 3000 TG 50 thermobalance, which was calibrated using alumel, mumetal and trafoperm whose respective Curie points were 149.00, 393.66 and 744.00 °C. About 10 mg of each sample were heated from 50 °C to about 600 °C at a rate of 10 K/min in synthetic air or nitrogen.[**] Gas flow rates of 100 ml/min were used. To pin point the peak temperatures, step analyses of the profiles using

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[**] 10 K/min is a convenient and suitable heating rate for characterization of thermal behaviour of macromolecular compounds.

the DTG facilities of the Mettler TA 3000 were carried out.

The DSC measurements were carried out with a Mettler TA 3000 DSC 20, which was calibrated with ultra pure indium (99.999 %) whose temperature of fusion was recorded as 155.8 °C. Sample amounts of about 10 mg were heated at 6 K/min in air or nitrogen from 50 °C to 600 °C using purge gas velocities of 50 ml/min.

RESULTS AND DISCUSSION

The TG and their corresponding time derivatives (DTG) curves as well as the DSC curves of the ABS, PS and SAN samples in air and nitrogen are given in Fig. 1, Fig. 2 and Fig. 3 respectively. The TG results are summarized in Table 1.

TABLE 1

Results of TG analysis of ABS, PS and SAN plastics in air and nitrogen at 10 K/min and gas flow of 100 ml/min.

Plastic	Purge gas	Peak number	Temperature range (°C)	Peak temperature (°C)	Weight loss (%)
ABS	air	1	300 - 450	404	89
		2	450 - 600	532	11
	nitrogen	1	357 - 487	423	96
PS	air	1	260 - 424	392	98
	nitrogen	1	304 - 454	418	99
SAN	air	1	205 - 430	403	91
	nitrogen	1	340 - 446	416	97

One of the most fundamental concepts in thermal degradation of plastics is the presence or absence of oxygen during the decomposition process. In all cases, decomposition of the plastics studied occurred at a lower temperature for decomposition in air than in nitrogen. This is suggestive of different decomposition mechanisms in the two atmospheres and is supported by the different DSC profiles obtained in the two atmospheres for each polymer. Oxidative decomposition has been shown to occur at a lower temperature than non-oxidative decomposition [21-23]. This has been attributed to the easier occurrence, presumably on energetic grounds, of oxidative reactions than other reaction types. Oxygen reacts with the polymer molecules and is known to penetrate polymer films. The rate of penetration becomes slower in the interior of the film.

ABS and SAN have been noted to display large endothermic peaks around 380 °C, which are characteristic of styrene containing polymers [24,25]. In both air and nitrogen each of the polymers had an endothermic peak around this temperature region, as can

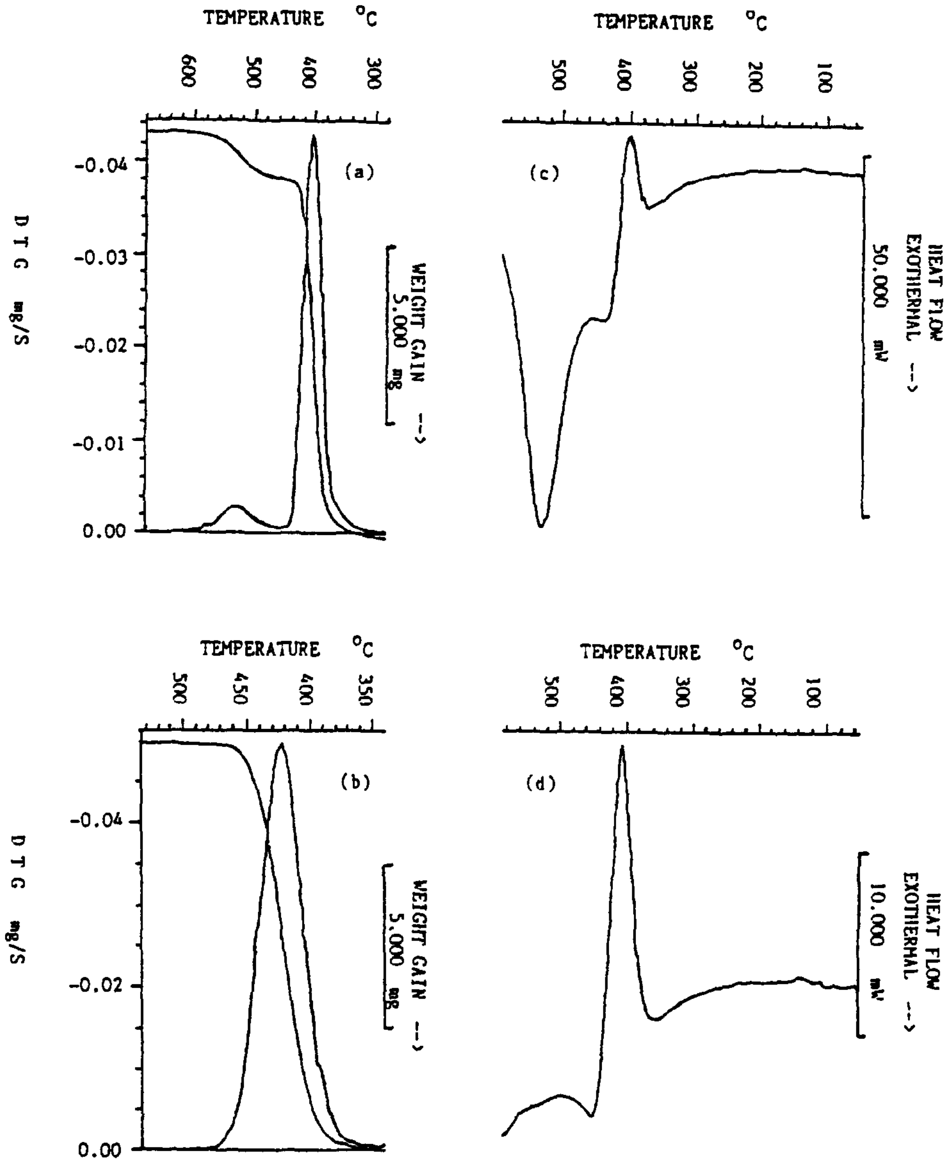

Fig. 1. TG and DTG curves of ABS in (a) air and (b) nitrogen at a heating rate of 10 K/min and gas flow rate of 100 ml/min; and corresponding DSC curves in (c) air and (d) nitrogen at a heating rate of 6 K/min and gas flow rate of 50 ml/min.

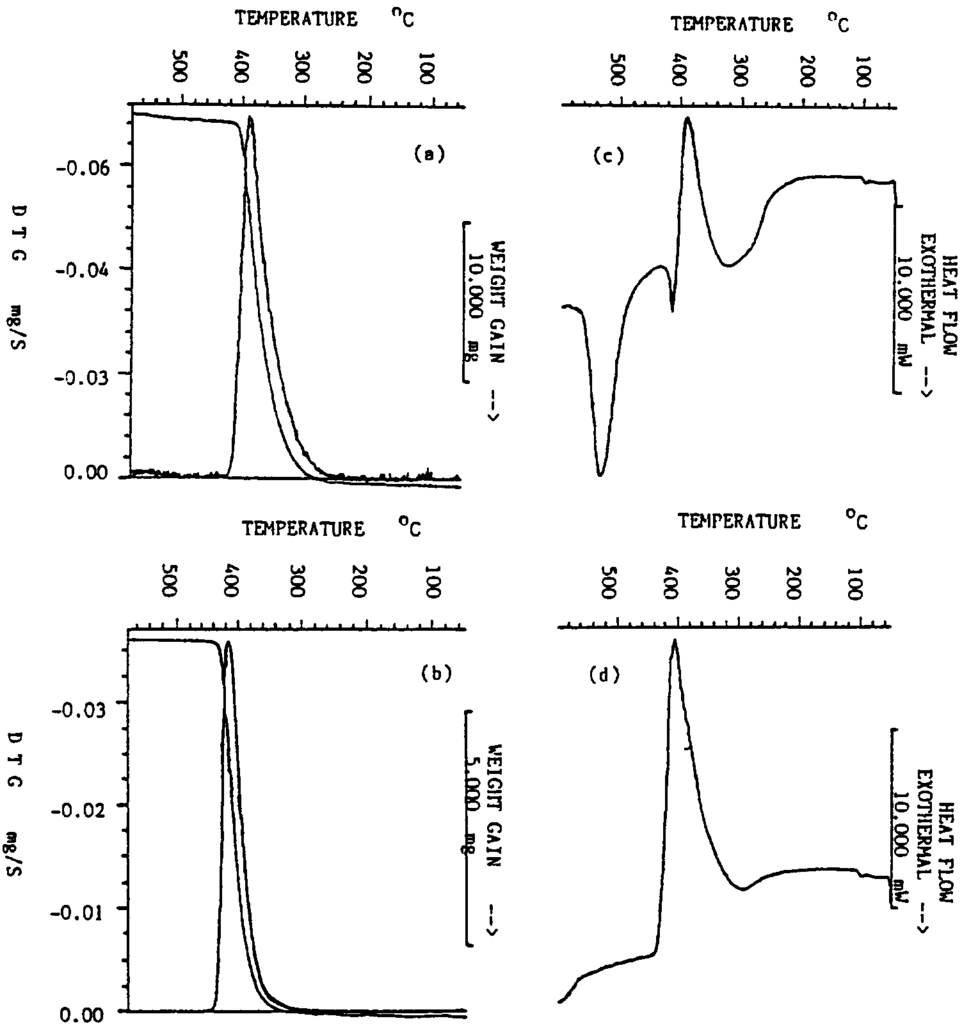

Fig. 2. TG and DTG curves of PS in (a) air and (b) nitrogen at a heating rate of 10 K/min and gas flow rate of 100 ml/min; and corresponding DSC curves in (c) air and (d) nitrogen at a heating rate of 6 K/min and gas flow rate of 50 ml/min.

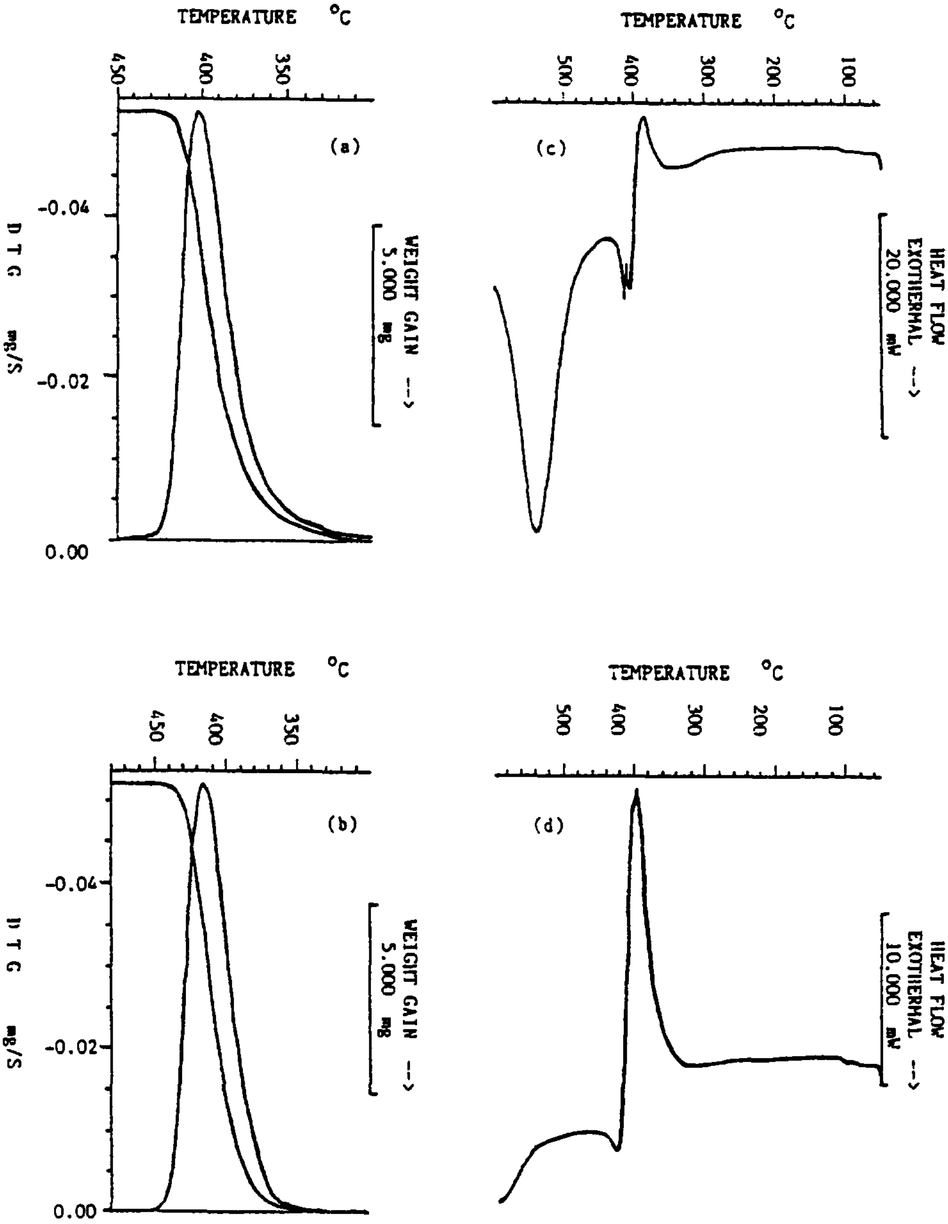

Fig. 3. TG and DTG curves of SAN in (a) air and (b) nitrogen at a heating rate of 10 K/min and gas flow rate of 100 ml/min; and corresponding DSC curves in (c) air and (d) nitrogen at a heating rate of 6 K/min and gas flow rate of 50 ml/min.

be seen from the figures. The decomposition in air for each of the polymers studied can be said to have occurred by a more complex process, which is revealed by the presence of large exothermic peaks above 400 ℃, than in nitrogen. Each DSC curve is characterized by small peaks around 100 ℃. Since there was no loss in weight recorded around this temperature, the changes can be attributed to physical changes such as melting of the plastic or loss of water of crystallization. No further enthalpy changes were observed until after 200 ℃.

Some interesting thermal stability studies of an ABS plastic using TG and differential thermal analysis (DTA) in static air have been presented [15,17]. Two decomposition steps were noted. The ABS sample studied in these experiments also displayed a two step decomposition in dynamic air. This is in contrast to decomposition in nitrogen which had only one step. The first step for decomposition in air occurred over a temperature range of about 150 ℃. It started at about 300 ℃ and ended at about 450 ℃. Its peak occurred at 404 ℃. During this step 89 % of the sample was converted into volatile compounds. The second decomposition, during which the remaining 11 % of the sample volatilized, started at about 450 ℃ and was complete at about 600 ℃, giving a decomposition temperature range of 150 ℃. Its peak occurred at 532 ℃. Decomposition in nitrogen started at about 357 ℃ and ended at about 487 ℃, giving a decomposition temperature range of 130 ℃. The decomposition kinetics of ABS are well documented [15,17,26,27]. Petrovic et al. have given an in depth general account on determination of kinetic parameters of plastics from TG and DSC measurements [28].

In both air and nitrogen the PS sample of this study had a one step decomposition. In air, decomposition started at about 260 ℃ and was complete at about 424 ℃, giving a decomposition temperature range of about 164 ℃, during which the sample was 98 % decomposed. The peak decomposition temperature was 392 ℃. In nitrogen, decomposition began at about 304 ℃ and was complete at about 454 ℃, giving a decomposition range of 150 ℃. Sample decomposition was 99 % and the peak decomposition temperature was 418 ℃. The results obtained for decomposition in nitrogen compare well with those obtained by MacNeill, who had a decomposition onset of about 300 ℃ and a peak decomposition temperature of 420 ℃ [29]. Kinetics of thermal decomposition of PS have been presented in a vast number of papers. Notable thermal analysis studies of PS include those of Cameron et al. who simulated isothermal plots of various PS types using a four-parameter equation [30]. Kishore noted that although degradation of PS occurs at a lower temperature in an oxygen containing atmosphere than a nitrogen one, the rate of maximum degradation is higher in nitrogen than in the presence of oxygen [31].

Thermal analysis studies of SAN have been discussed by a number of authors [3,24,32,33,34]. The SAN sample of this study had a one step decomposition in both air and nitrogen. Decomposition in air started at about 205 ℃ and was complete at about 430 ℃ giving a decomposition temperature range of 225 ℃ during which approximately 91 % of the sample was converted into volatile products. The peak decomposition temperature was 403 ℃. In nitrogen decomposition began at about 340 ℃ and was complete at about 446 ℃ giving a decomposition temperature range of 126 ℃. Sample decomposition was recorded as 97 % at a peak temperature of 416 ℃. Comparing the peak decomposition temperature of 416 ℃ for SAN in nitrogen with the 425 ℃ obtained by Luda di Cortemiglia et al. [26], under similar experimental conditions, gives a difference of 9 ℃. If this difference is regarded as significant and is not blamed on inter-laboratory variations a possible explanation would be sample difference, such as molecular weight and serves to underscore the need to characterize the sample one is dealing with.

CONCLUSION

A combination of TG and DSC analysis of the ABS, PS and SAN samples under study revealed that no significant decomposition chemical changes occur below 200 ℃.

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