Influence of Flame Retardant Additives on the Processing Characteristics and Physical Properties of ABS

Richard Seddon, John F. Harper*

Institute of Polymer Technology and Materials Engineering, Loughborough University Loughborough, Leicestershire, LE11 3TU, UK

SUMMARY: Antimony trioxide (Sb_2O_3) is a common additive in flame retardant formulations and a study has been made to determine the effects of adding different grades into ABS polymer either alone or with commercial brominated materials bis(Tribromophenoxy)ethane (BTBPE) or Tetrabromobisphenol A (TBBA). The results consider mechanical, microscopical and flame retardant properties, and the effects of different Sb_2O_3 grades with average particle sizes of 0.1µm, 0.52µm and 1.31µm. The Sb_2O_3 was added at 4wt% loadings and the bromines at 20wt% loadings.
Additions of different grades of antimony trioxide showed that standard grades (0.52 and 1.31µm) had a detrimental effect on impact and flexural properties when added at a 4wt% loading. The use of a new sub-micron particle size product (0.1µm) had little effect on impact properties and only a slight detrimental effect on the flexural modulus and flexural strength when added to the ABS.
Additions of either of the two brominated materials also caused a large drop in impact properties when added at 20wt% loadings. The addition of TBBA BA-59P into ABS caused an increase in both flexural modulus and flexural strength which was contrary to expectations. When formulated with 4wt% 1.31µm Sb_2O_3 these bromine containing compounds suffered a further reduction in impact energies. Using the 0.1µm material improved both impact and flexural properties but impact values were still below those of unfilled ABS. The addition of the 0.1µm grade resulted in improvements in fire resistance as measured by the UL-94 properties.

Introduction

Antimony trioxide and halogens form one of the more effective flame retardant packages available for polymer systems[1]. This package is traditionally used in acrylonitrile-butadiene-styrene (ABS) polymers. Many FR-ABS compounds are utilised in home and business electrical equipment, communications products as well as car interior trims and panels, where good impact properties are required. The physical characteristics of these flame retarded grades have become more important because of the trend to move towards lighter, thinner-walled products for modern appliances. Due to these dimensional changes, material properties of the FR-ABS grades must improve in order to maintain standards. The presence of both antimony and halogens however can cause large reductions of the mechanical properties, particularly impact values. It is this problem that is addressed by the work in this paper.

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Experimental

The base ABS polymer used in this work was Cycolac T produced by GE Plastics. This is a general purpose injection mouldable grade with impact properties in the middle of the ABS range. Three antimony trioxide grades were supplied by Anzon Ltd. (Great Lakes Chemicals) and had the following average particle sizes: Timonox® Red Star (1.31μm), Microfine A05 (0.52μm) and sub-micron antimony trioxide (0.1μm). The particle sizes of all three grades were analysed by Anzon Ltd. using a Horiba LA-900 laser sizing device and the particle size distributions are shown in Figure 1. Two melt blendable brominated materials were supplied in powder form by Great Lakes Chemical (Europe) Ltd. and were: 1,2-bis(tribromophenoxy)ethane (FF680™) and tetrabromobisphenol A (BA-59P™). Ten formulations as detailed in Table 1 were compounded. These were produced using an APV twin screw co-rotating compounder with a screw diameter of 30mm and an L/D ratio of 30:1, calibrated to maintain a constant output of 12kg/hr. A Negri Bossi NB62 injection moulder was used to mould notched impact, flexural and Limiting Oxygen Index[2)] and Underwriters Laboratory UL-94[3)] flame test bars. Samples of all the compounded formulations were titrated to determine Sb_2O_3 content[4)].

Impact properties were measured using a Rosand Instrumented Falling Weight impact tester with a mass of 26.2kg and an impact velocity of 3m/s. The sharp notched impact bars were tested in the Charpy mode using a span of 40mm. Peak force, peak and failure energy and peak and failure deflection were recorded using the appropriate software. Flexural strength and modulus were measured at room temperature using a Lloyd universal test machine with a three-point bend jig. LOI flame bars (120mm x 6.4mm x 3.0mm) and UL-94 flame bars (127mm x 12.7mm x 1.6mm) were deburred and conditioned prior to testing. Analysis of fracture surfaces as well as determination of the size and dispersion of the fillers in the ABS was carried out using a Cambridge/Leica SEM Stereoscan 360 instrument. TEM samples were cut to size, stained using osmium tetroxide (OsO_4) and then sectioned using a glass microtome. Filler dispersion and location were determined using a Jeol 100CX instrument.

Particle sizing

All components of the formulations (excluding the sub-micron grade) were chosen as representative materials of those currently used in the industry. The sub-micron grade was a new product and particle sizing was carried out to analyse the size distribution of the material. Figure 1 shows the distribution curves for the three antimony trioxide grades. The most noticeable feature about the curves is the second peak (~0.25µm) on the 0.10µm grade curve. This is caused by the presence of small amounts of agglomerate fragments which remained after the milling process. These fragments were not noticeable in TEM sections of the compounded formulations which suggests that they broke down during the compounding.

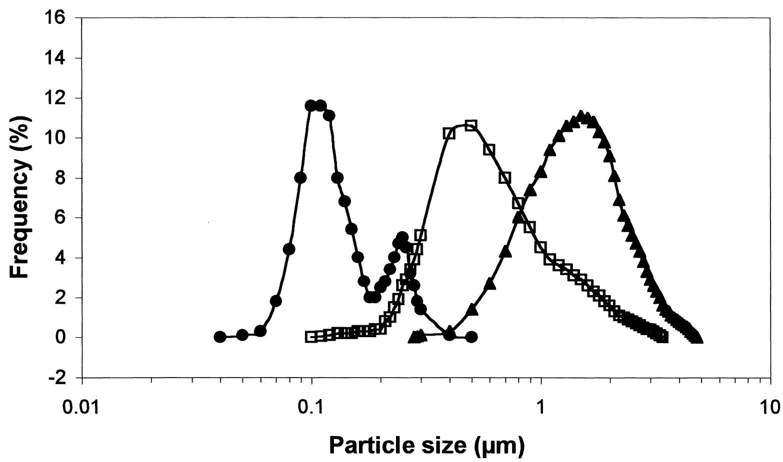

Figure 1. Particle size distributions of the three Sb_2O_3 grades.

—●— 0.10µm —□— 0.52µm —▲— 1.31µm

Compounding

Table 1 shows the ten compounds processed.

Table 1. Formulations compounded and studied in this work (weight%).

Formulation	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Cycolac T	100	96	96	96	80	80	76	76	76	76
Timonox® Red Star (1.31μm)		4					4	4		
Microfine A05(0.52μm)			4							
Sub-micron Sb_2O_3 (0.10μm)				4					4	4
BTBPE FF680					20		20		20	
TBBA BA-59P						20		20		20

All formulations were compounded at a constant output of 12kg/hr and screw speed of 170 rpm. The presence of 4wt% Sb_2O_3 (formulations 2, 3 and 4) reduced torque and die head pressures slightly whilst improving melt stability over unfilled Cycolac T. The decreasing size of the Sb_2O_3 particles did not appear to make any difference to the readings. Additions of the two bromines (5 and 6) lowered torque and pressure values further to the detriment of the melt, which became unstable. This caused thinning of the melt prior to entering the cooling bath which resulted in occasional strand breakage. The additional presence of 4wt% 1.31μm Sb_2O_3 to the bromines (formulations 7 and 8) had no further effect on the readings but did improve the melt strength. The use of 0.1μm Sb_2O_3 material in 9 and 10 improved melt strength but had no further effect on either torque or pressure readings.

Results

Table 2 shows the impact and flexural results for all ten compounds as well as their antimony trioxide contents.

Table 2. Mechanical properties and Sb_2O_3 contents of formulations.

	Sb_2O_3 content (wt%)	Peak Impact Energy (J)	Peak Impact Deflection (mm)	Failure Impact Energy (J)	Flexural Modulus (N/mm^2)	Flexural Strength (N/mm^2)
1	-	0.56 (0.03)	1.65 (0.05)	1.24 (0.05)	2223 (44)	67.4 (0.8)
2	3.2	0.30 (0.04)	1.11 (0.37)	0.85 (0.04)	2197 (44)	63.7 (0.5)
3	5.5	0.41 (0.05)	1.49 (0.08)	0.92 (0.05)	2255 (12)	63.6 (0.5)
4	3.5	0.51 (0.04)	1.64 (0.07)	1.20 (0.09)	2310 (40)	63.9 (0.6)
5	-	0.39 (0.07)	0.88 (0.35)	0.96 (0.06)	2131 (44)	60.1 (0.7)
6	-	0.28 (0.04)	1.06 (0.21)	0.85 (0.06)	2547 (23)	67.3 (0.7)
7	4.1	0.24 (0.04)	1.09 (0.18)	0.78 (0.06)	2150 (22)	57.3 (0.7)
8	3.8	0.23 (0.01)	1.13 (0.02)	0.70 (0.08)	2619 (34)	65.8 (0.9)
9	3.5	0.29 (0.04)	1.34 (0.13)	0.86 (0.03)	2326 (33)	59.7 (0.6)
10	3.6	0.47 (0.01)	1.68 (0.02)	0.77 (0.03)	2802 (24)	70.5 (0.5)

The addition of 3.2wt% 1.31μm Sb_2O_3 reduced impact failure energies by 30% compared to unfilled ABS; the addition of 5.5wt% 0.52μm reduced the property by 25% and most significantly the addition of 3.5wt% 0.1μm reduced the impact energies by only 3%. The higher loading level in formulation 3 (0.52μm) most likely explains the reason why the failure energy results between the 0.52 and 1.31μm formulations are similar (considering deviations). Despite this however, decreasing the particle size can be shown to improve impact properties[5)].

Figure 2 summarises the peak and failure impact energies and Figure 3 shows the flexural modulus and flexural strength values for all ten formulations.

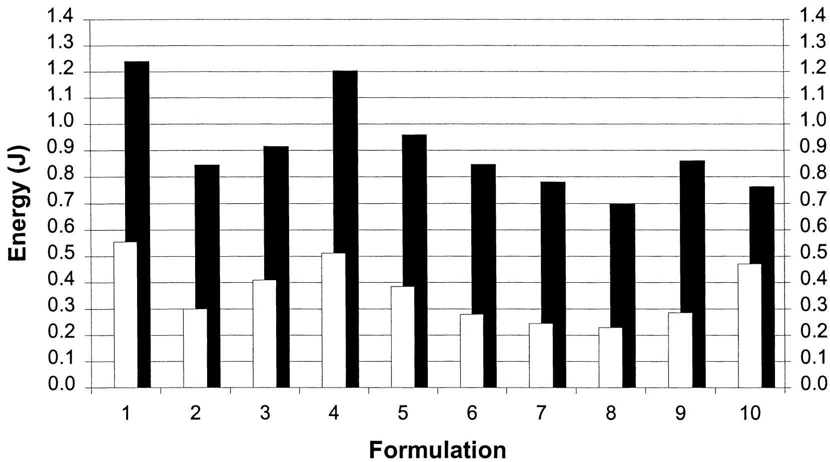

Figure 2. Sharp notched impact bar results - peak and failure energies.

■ Failure Energy □ Peak Energy

SEM and TEM analysis of samples from these formulations showed some clustering of particles in formulations containing the 1.31μm and 0.52μm Sb_2O_3 grades which resulted in clusters (not agglomerates) approximately 1 to 3μm across. The dispersion and distribution of the antimony trioxide was superior in the 0.1μm grade formulation. This suggested that the improvements in the impact properties could be attributed to both decreasing particle size and to some extent, improved dispersion of the antimony trioxide within the ABS.

TEM analysis showed that in all three cases the antimony trioxide was found in the SAN phase of the ABS polymer. Also seen within these formulations was the change in the number of cavitated butadiene particles and the number of crazes occurring in the filled compounds. Crazing is known to occur ahead of the crack tip and helps to dissipate energy during fracture and the fact that less crazing and cavitation was seen in the filled compounds (2,3 and 4) suggested an explanation for the reduced impact energies. The sub micron filled compound had reduced amounts of crazing compared to unfilled ABS (see Plates 1 and 2). The number of crazes and cavities decreased with increasing particle size.

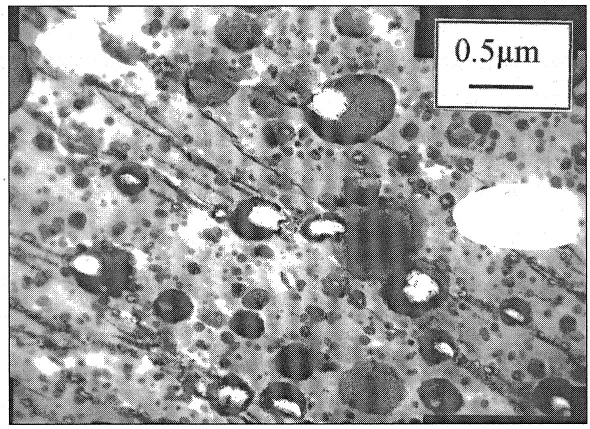

Plate 1: TEM section of unfilled ABS.

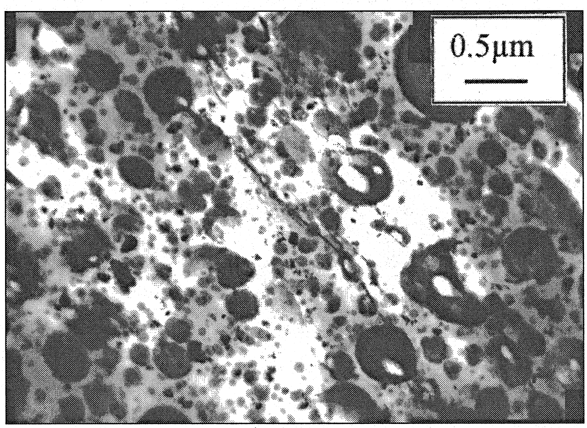

Plate 2: TEM section of 0.10µm filled ABS.

All three antimony grades lowered flexural strength, but the flexural modulus increased with decreasing particle size. Flame properties of all three antimony formulations were poor (see Table 3). This was expected due to the fact that antimony trioxide has only a slight flame retardant effect when used on its own.

The individual additions of 20wt% BTBPE FF680 and 20wt% TBBA BA-59P resulted in a drop in failure energies of 25% and 30% respectively (when compared to unfilled ABS).

Reductions in both flexural modulus and strength were caused by the BTBPE FF680 but the TBBA BA-59P caused an increase in both properties. This phenomenon has also been noted by other researchers[6)]. TEM analysis could not determine the location of the bromine in the final compound due to insufficient staining of the bromine by the osmium tetroxide (OsO_4). Use of a more aggressive staining agent, ruthenium tetroxide, also failed to determine the location. STEM analysis and X-ray mapping at several locations in both samples suggested a blanket effect of bromine across the samples with a slight increase in concentration at the butadiene/SAN interface.

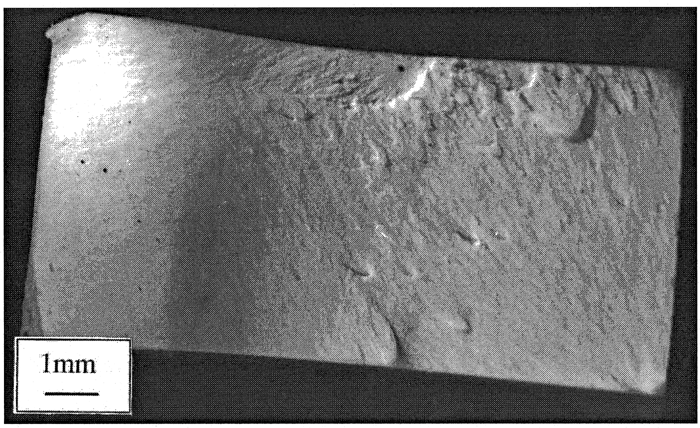

Plate 3: Fracture surface of 0.10μm Sb_2O_3 filled ABS.

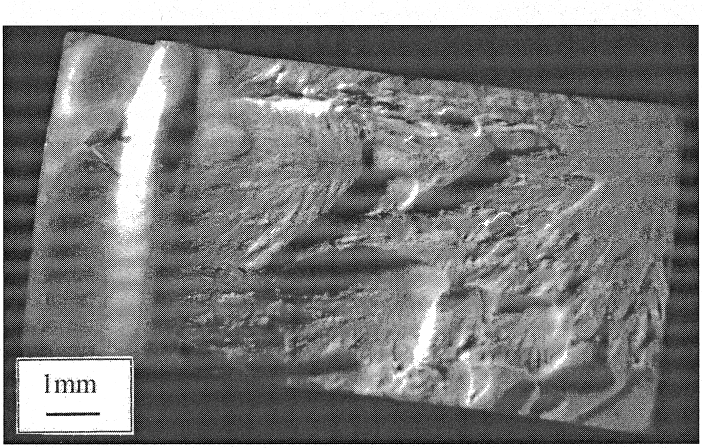

Plate 4: Fracture surface of Br/Sb_2O_3 (0.10μm) filled ABS.

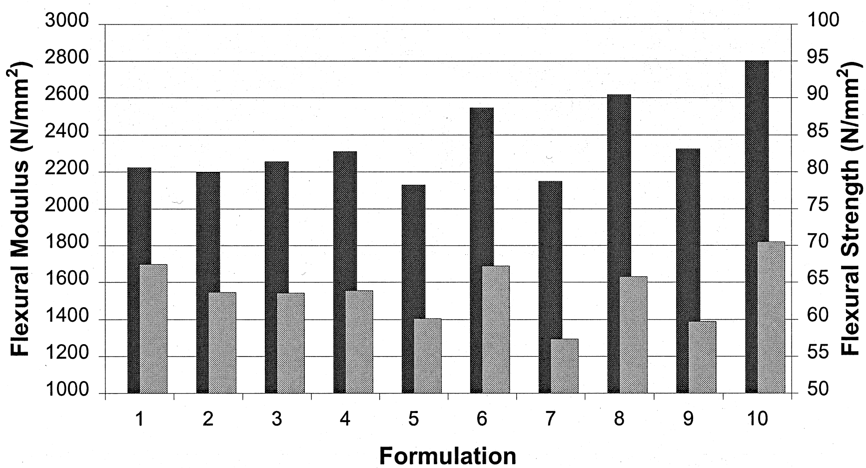

Figure 3. Flexural modulus and flexural strength values

■ Flexural Modulus ▒ Flexural Strength

Incorporation of 4wt% 1.31µm Sb_2O_3 with the two bromines (Formulations 7 and 8) caused a further drop in both peak and failure impact energy. This was expected as both additives had each caused a drop in these properties when added individually. The effect the presence of a bromine has on the impact properties is clearly shown in the fracture surfaces in Plates 3 and 4. Flexural characteristics followed the same pattern seen in the previous formulations. LOI test results for these formulations were good but the samples did not achieve a V0 UL-94 reading as might have been expected. This was due to several of the samples dripping.

Table 3. LOI and UL-94 flame properties.

Formulations	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
LOI	18.3	18.7	18.4	18.2	20.2	20.5	29.0	29.0	26.5	27.5
UL-94	FAIL	FAIL	FAIL	FAIL	V2	V2	V2	V2	V0	V2
Burn time(s)[a)]	>250	>250	>250	>250	200	195	60	50	23	36

[a)] Total time for 10 samples

The presence of the 0.1μm Sb_2O_3 in formulations 9 and 10 resulted in impact energies which were 10% higher than those values obtained for the formulations containing 1.31μm Sb_2O_3 and a bromine. These new 0.1μm formulations had energies between 70% and 75% of the values of unfilled ABS. Similar improvements were seen with the flexural properties. LOI test values were reduced slightly, which was most likely due to the presence of the binder resin in the 0.1μm material. Using the 0.1μm grade of antimony trioxide resulted in an improvement in UL-94 values with a total burn time for all 10 test bars in formulations 9 and 10 lower than the times for formulations 7 and 8. The binder resin left Formulation 10 susceptible to dripping and two samples failed in this manner which resulted in a V2 rating. Total burn time for this formulation is better than that of the corresponding 1.31μm formulation (number 8).

Conclusions

Additions of 20wt% brominated material lowered the viscosity of the polymer melt to a point where it became unstable. The addition of 4wt% Sb_2O_3 with 20wt% Br did not alter the viscosity but did improve melt strength.

The use of sub-micron particle size (0.1μm) antimony trioxide grades in ABS improved impact properties when compared to the values obtained using standard particle size grades (0.52 and 1.31μm).

Using 20wt% BTBPE FF680 resulted in better impact properties than when using 20wt% TBBA BA-59P, although the BA-59P imparted greater flexural modulus and flexural strength.

Flame properties (in particular UL-94) appeared to be better in formulations containing the smallest particle sized antimony grade (0.1μm).

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