

USING MICRO- AND NANO-COMPOSITE APPROACHES TO IMPROVE FLAME RETARDANCY OF ABS

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Abstract

The first purpose of this study was using micro-composite approach by investigating the effects of micron-sized zinc borate (ZB) on the flammability behavior of ABS when used with and without a traditional brominated flame retardant (BFR) / antimony trioxide (AO) system. The second purpose was using nano-composite approach by investigating the contribution of nanoclays (NC) to the flame retardancy performance of the same systems. Flame retardancy of the specimens was investigated by Mass Loss Cone Calorimeter, Limiting Oxygen Index measurements and UL-94 vertical burning tests. Studies indicated that flame retardancy parameters were kept when AO were replaced with ZB , while use of nanoclays improved all parameters significantly. Residue analyses revealed that predominant flame retardancy mechanism of traditional system was gas phase action, while ZB especially acts in the condensed phase by forming thicker and stronger char layer. Nanoclays further contribute to the formation of stronger and carbonaceous- silicate char acting as a barrier to heat and flammable gases and retarding volatilization via tortuous pathway.

1 Introduction

Acrylonitrile butadiene styrene (ABS) is widely used in automotive parts and electrical/electronic appliances. Due to its high level of flammability a number of traditional flame retardants are utilized. In this respect, binary compounds of brominated flame retardants with antimony trioxide are one of the most effective systems.

As the micro-composite approach, there are several studies utilizing micron sized zinc borate (ZB) to improve fire performance of polymers such as PA, EVA, LDPE, PVC and PC. However, there seems to be no work studying the use of ZB in ABS. Since ZB is an effective smoke suppressant and much cheaper than antimony trioxide (AO), it would be beneficial at least to replace certain amount of AO with ZB.

As the nano-composite approach, there are few numbers of researches examining the effects of nanoclays on the cone calorimetric flammability behavior of ABS [1-4]. These studies indicate that insertion of nanoclay in ABS matrix improves flame retardancy of ABS at some extent. Due to the structure of layered silicates having nanometer-scaled thickness and high aspect ratio, nanoclays even with low loading levels lead to effective barrier properties by entrapment of active radicals and inhibiting flow of flammable gases which results in efficient condensed phase flame retardancy.

2 Materials and Testing Methods

Acrylonitrile butadiene styrene (ABS) used as the matrix polymer was an injection molding grade (BASF, Terluran GP-22) with a density of 1.04 g/cm³. As the traditional flame retardant system, combinations of three different components were used. These were; aromatic brominated compound (BFR) ethane-1,2-bis pentabromophenyl (Albemarle, Saytex 8010) with an average particle size of 5.6 μm, antimony trioxide (AO) having particle size range of 0.3-1.1 μm, with 99% purity, and zinc borate (ZB) (Eti Mine Works Inc., Turkey) with an average particle size of 12.4 μm and 97% purity. Finally, the nanoclay (NC) used was Cloisite 10A (Southern Clay) an organically modified montmorillonite with dimethyl benzyl hydrogenated tallow quaternary ammonium.

Polymer compounds, micro- and nano-composites were produced by melt mixing method in a laboratory size twin-screw extruder (Rondol Microlab 10 mm, L/D = 20). Temperature profile during extrusion was kept as 165°C -195°C -200°C -210°C - 200°C with 60 rpm screw speed. Specimens were shaped by two methods; compression and injection molding. Square specimens of mass loss calorimeter test having 100x100x4 mm dimensions were compression molded at 200°C with 5 minutes preheating and 100 bar pressure application for 1 minute. Injection Molding (DSM X-plore 10cc Micro Injection Molder) of the LOI and UL-94 flammability test specimens were done with barrel and mold temperatures of 220°C and 40°C, respectively under three step pressure of 10 bar.

Flame retardancy of the specimens was investigated by using three methods. In the first one, Limiting Oxygen Index (LOI) measurements were conducted according to ISO 4589 on an FTT (Fire Testing Technology Inc.) oxygen index apparatus. Secondly, UL-94 vertical burning tests were assessed as the procedure explained in UL-94 standards. As the third method, Mass Loss Calorimeter (Fire Testing Technology Inc.) was utilized to measure heat release rates and mass loss rates of the burning specimens according to the procedure explained in ISO 13927. During Mass Loss Calorimeter (MLC) test, external heat flux was kept as 35 kW/m² and data were recorded using a data-acquisition system. Details of the other analyses conducted are explained in our previous work [5].

3 Results and Conclusions

Wide angle X-ray diffraction analysis (XRD) of the nanocomposite specimens in Figure 1 shows that loading 5% NC into ABS matrix resulted in three peaks. The first sharp peak at $2\theta=2.95^\circ$ corresponds to the interlayer spacing of 3.0 nm. Since the initial d-spacing of nanoclay (Cloisite 10A) is 1.9 nm, increase of gallery distance to 3.0 nm indicates that silicate layers are very well intercalated by the ABS molecular chains. The second and third peaks (at $2\theta=5.70^\circ$ and $2\theta=8.83^\circ$, respectively) are rather broad with low intensity. These peaks could be due to the second order and third order reflections corresponding to the same d-spacings (3.1 nm and 3.0 nm, respectively) with first order reflection.

XRD diffractograms of the nanocomposites with flame retardants (BFR, AO and ZB) also show that, first peak and third peak almost disappear. This could be due the attenuation and absorption of the reflections by the high amount of elements in the flame retardant compounds (such as bromine, antimony, zinc, etc) having high level of absorption coefficients.

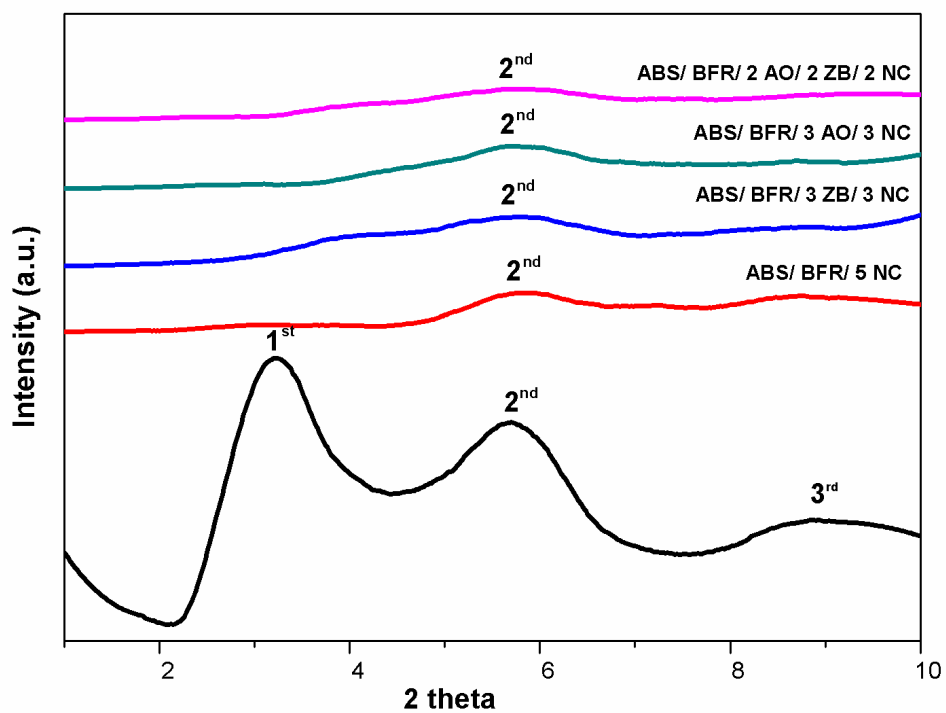


Figure 1. XRD diffractograms of the specimens.

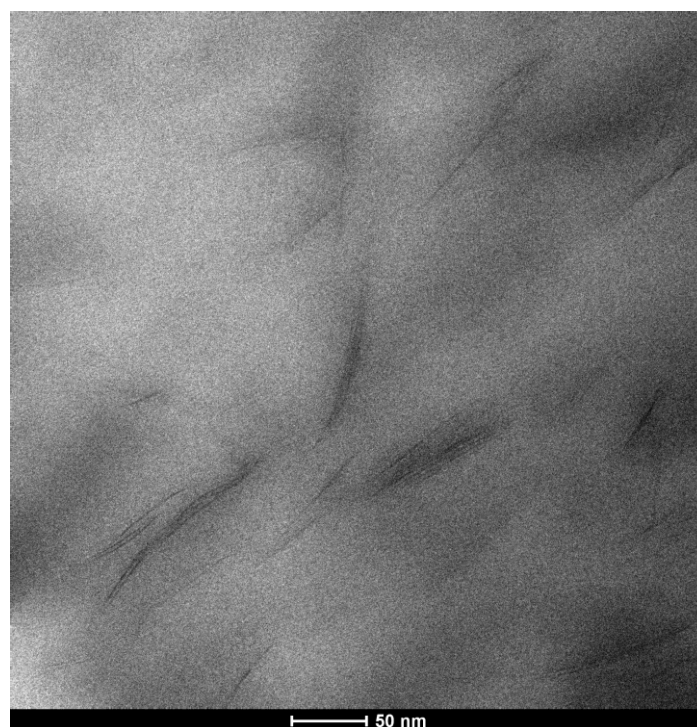


Figure 2. TEM image of ABS/ 5 NC specimen showing intercalated and partly exfoliated NC layers.

In order to reveal XRD results, specimens were also investigated under transmission electron microscopy (TEM). TEM image of ABS/ 5 NC specimen in Figure 2 confirms the XRD pattern of this specimen indicating intercalation of silicate layers with certain level of exfoliation. TEM studies of the nanocomposites with flame retardants showed that there is no significant difference in terms of the intercalated/ partly exfoliated structure of silicate layers.

Results of UL-94 and LOI flammability tests are tabulated in Table 1 while Figure 3 gives heat release rate curves obtained from the mass loss calorimeter (MLC). These results simply show that ABS has failed ranking of UL-94 vertical burning test, considerably low LOI value of 19%, and very high Peak Heat Release Rate (PHRR) of 900 kW/m².

When only 5% NC was introduced into ABS matrix, PHRR decreased from 900 to 609 kW/m². This 32% suppression in PHRR value could be attributed to intercalation of silicate layers leading to barrier effect during combustion which inhibits flow of heat and flammable gases. However, slight increment in LOI value (20%) and failed ranking of UL-94 test indicated that use of NC alone leads to no significant flame retardancy behavior.

However, use of NC together with traditional brominated flame retardant (BFR/NC binary system) with BFR:NC ratio of 18:5 resulted in 66% suppression in PHRR value, improved LOI value to 24% and the best V-0 rating in UL-94 test revealed a much higher level of flame retardancy. This improved flame retardancy of BFR/NC system could be attributed to a combination of well-known gas and condensed phase flame retardancy mechanisms of traditional BFR and additional effective barrier properties of NC.

In the polymer industry, brominated flame retardants are usually used together with antimony trioxide (AO) acting as a very efficient synergist. Table 1 and Figure 3 show that traditional binary BFR/AO flame retardant system with BFR: AO ratio of 3:1 resulted in excellent flame retardancy data. That is, the highest rating of V-0 in UL-94 test, a very high LOI value of 30%, and a very large amount of suppression (73%) in PHRR. When half of the synergist AO was replaced with NC, i.e. the ternary BFR/AO/NC system with BFR:AO:NC ratio of 6:1:1 resulted in even slightly higher level of flame retardancy by increasing LOI value to 32% with preserved V-0 UL-94 rating and 74% reduced PHRR value. Indeed, the highest LOI value in this study was observed for this ternary BFR/AO/NC system.

BFR is capable of scavenging H• radicals in the gas phase which results in release of hydrogen bromide (HBr) and also promotes charring in the condensed phase. Moreover, insertion of AO with BFR results in better gas phase flame retardancy by forming antimony tribromide (SbBr₃) which is more active radical scavenger than hydrogen bromide. Therefore, just like in the previous group, the contribution of NC to the very efficient gas phase flame retardancy of BFR/AO binary should be its additional barrier effects.

Compared to neat ABS, the binary BFR/ZB system with BFR:ZB ratio of 3:1, LOI value increased from 19% to 23%, the suppression in PHRR decreased from 900 to 359 kW/ m² (40%), but UL-94 rating was fail. On the other hand, when NC is added to that compound, i.e. the ternary BFR/ZB/NC system with BFR:ZB:NC ratio of 6:1:1, then, this nanocomposite resulted in V-0 rating in UL-94 test, much higher suppression in PHRR value (68%) and more

Specimen Designation	UL- 94 rating	LOI (%O ₂)
ABS	Fail	19
ABS/ 5 NC	Fail	20
ABS/ BFR/ 5 NC	V0	24
ABS/ BFR/ 6 AO	V0	30
ABS/ BFR / 3 AO/ 3 NC	V0	32
ABS/ BFR/ 6 ZB	Fail	23
ABS/ BFR/ 3 ZB/ 3 NC	V0	24
ABS/ BFR/ 3 AO/ 3 ZB	V0	29
ABS/ BFR/ 2 AO/ 2 ZB / 2 NC	V0	30

Table 1. Specimen designation and results of UL-94 and LOI flammability tests.

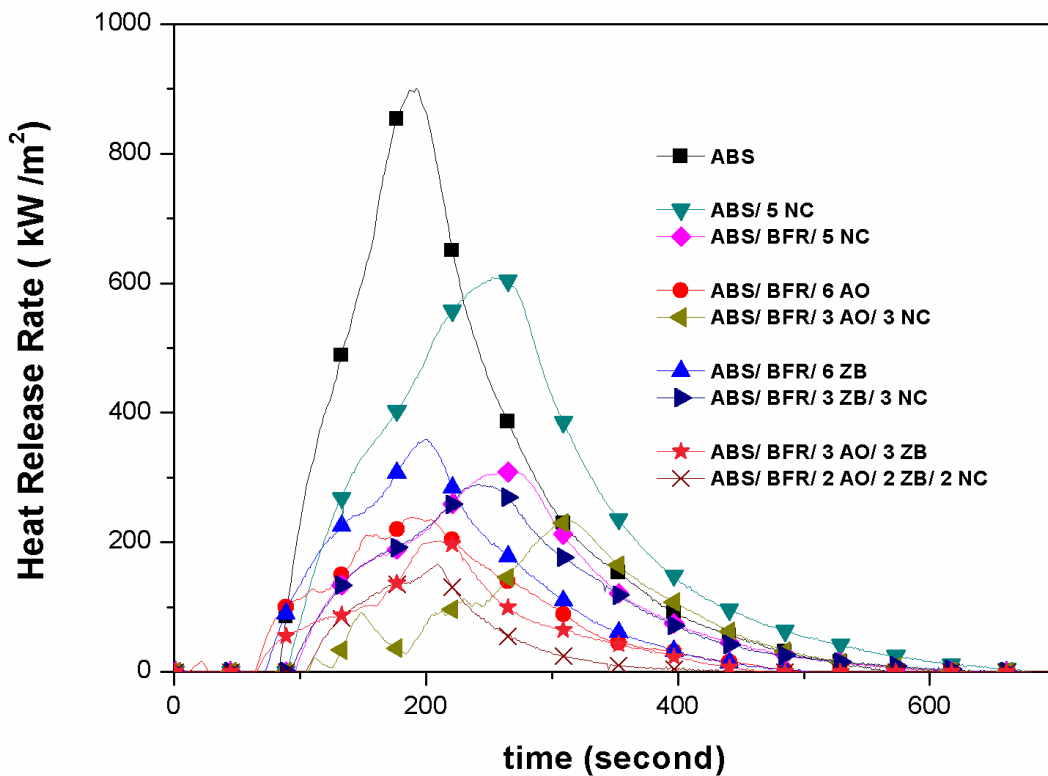


Figure 3. Heat Release Rate curves of the specimens.

improved LOI value (24%). By releasing chemically attached water molecules, ZB dilutes the flammable gases and also forms protective char layer inhibiting flow of heat and flammable gases leading to condensed phase flame retardancy mechanism. Therefore, effective barrier properties of NC could further improve condensed phase action of ZB resulting in a higher level of flame retardancy behavior.

Specimen of BFR/AO/ZB ternary system (with BFR:AO:ZB ratio of 6:1:1) increased LOI to 29%, suppressed the PHRR by 77% and obtained V-0 rating in UL-94 test. Its nanocomposite specimen, i.e. addition of NC into this system with BFR:AO:ZB:NC ratio of 9:1:1:1 resulted in even more improvements by increasing LOI value to 30%, keeping V-0 rating in UL-94 test and a significant suppression of PHRR by 82%. Again, these improvements may suggest that stronger and thicker char formation resulting in efficient condensed phase flame retardancy has been achieved by the combined action of NC and ZB. Therefore, the overall improved flame retardancy of this specimen could be attributed to the condensed phase flame retardancy of NC and ZB, plus effective gas phase flame retardancy mechanism of BFR and AO.

It can be generally concluded that addition of NC improves all flame retardancy parameters of neat ABS or ABS filled with traditional BFR, AO and ZB flame retardant compounds. This contribution is especially due to the condensed phase flame retardancy mechanism of NC which contributes stronger and carbonaceous char formation acting as a barrier to heat and flammable gases as explained above.

Moreover, when NC is intercalated in the polymer matrix, there could be another contribution which is discussed as “nanoconfinement” in the literature recently. That is, decomposing radicals of the main chain of ABS could be entrapped (confined) in between the intercalated silicate layers of NC leading to some recombination reactions, and thus retarding the rate of evolution of radicals.

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