

PREPARATION OF HIGH IMPACT POLYSTYRENE (HIPS) WITH ENHANCED FLAME RETARDANT PROPERTIES

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Abstract

The main purpose of this study is to improve high impact polystyrene (HIPS) flame retardant which accomplishes V-0 level of UL-94 flame test standard. This study was successful in improving flame retardant properties for HIPS by adding suitable flame retardant in small content. Various flame retardants, bisphenol A bis-diphenylphosphate (BDP), 9,10-dihydro-9-oxa-10-phosphahenanthrene-10-oxide (DOPO), triphenyl phosphate (TPP), magnesium hydroxide (MH) and organically modified montmorillonite (OMMT) were studied by melt blending with HIPS to prepare the samples for combustion and mechanical properties test. It's obviously shown that 4 HIPS compounds which were prepared with quaternary ammonium salt modified MMT (3 phr), BDP (15 phr), DOPO (15 phr) and TPP (15 phr) were accomplished in V-0 of UL-94 rating. Thermal stability will be improved when adding flame retardant. However, the presence of flame retardant in HIPS may decrease impact strength and mechanical properties of HIPS.

1. Introduction

High impact polystyrene (HIPS) is a thermoplastic that is widely used for numerous applications in our daily life, for example, in transportation, packaging, electronics and appliances. HIPS is also known for their high flammability; mostly accompanied by the production of toxic gases and smoke during combustion. However, the improvement of the flame retardant behavior of this polymer and composites is a major challenge for extending their use in a wide range of applications. Therefore, for safety reasons and product concerns, one should be aware of not using any parts which are flammable.

Flame retardants (FR) are incorporated with polymers to improve flame resistance. FRs can act in a numerous means to provide fire resistance, for instances, by raising the ignition temperature; reducing the rate of burning; reducing flame spread; and reducing smoke generation [1]. Normally, Flame retardant that used with HIPS is halogen-containing compound combined with antimony [2, 3]. However, it led to environmental problems. Therefore, enormous efforts have been developed flame retardant systems which are halogen-

free such as organic phosphorus compounds, nanoclay, inorganic compound. The enhancement in flame retardancy with the incorporation of phosphorus can act in the condensed phase promoting char formation on the surface, which acts as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and air [4] and some also be active in the gas phase. Some phosphorus flame retardants are reactive FRs, which means they are chemically bound to a polymer. [5] The incorporation of a relatively low quantity of nanoclay in the polymer matrix creates a protective layer during combustion that effectively shields the underlying polymer and limits heat transfer into the material, volatilization of combustible degradation products and diffusion of oxygen into the material. [6, 7] Inorganic flame retardant such magnesium hydroxide is well established as an acid-free, halogen-free and smoke suppressing flame retardant. It decomposes endothermically and releases water at about 327 – 427 °C, so that the flame retardant effect is based on cooling and dilution [8].

In this research, the flame retardant property of high impact polystyrene was improved. A number of halogen-free flame retardant additives: three types of phosphate flame retardants, modified nanoclay, magnesium hydroxide were added to HIPS. Moreover, the mechanical properties of HIPS compounded with flame retardant were investigated.

2. Experimental

2.1. Materials

High Impact Polystyrene (HIPS) (830) was supplied by IRPC inc., 9,10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide (DOPO) and Bisphenol-A bis(diphenyl phosphate) (BDP) were obtained from Sunny Chemical Co. Ltd, Magnesium Hydroxide ($Mg(OH)_2$); (MH) was purchased from Ajax Finechem Pty Ltd, Triphenyl Phosphate (TPP) was purchased from Young's corporation and Organically modified montmorillonite (OMMT) was purchased from Connell Bros. company Ltd.

2.2. Sample preparation

HIPS was dried in the oven at 80 °C for 24 h before being processed to remove moisture. Then, HIPS and flame retardant were mixed by using a high speed mixer and then melt blend in a co-rotating twin-screw extruder. The temperatures of the extruder were 150-200 °C at screw speed 80 rpm then the pellets were fed into an injection machine to prepare the test specimens, the temperatures of which were 195, 200, and 210 °C.

2.3. Characterization and testing

Flammability test; The Underwriters Laboratories, UL-94 vertical test according to ASTM D3801. The Limiting Oxygen Index (LOI) according to ASTM D2863. *Thermogravimetric analysis*; Thermal degradation studies in oxygen were performed using a thermogravimetric analyzer (Mettler Toledo, Switzerland). The samples were heated from room temperature up to about 800 °C at a heating rate of 10°C /min. *Mechanical properties*; The impact strength of composites was measured by Izod pendulum impact testing machine according to ASTM D-256. The tensile properties were measured by Instron universal testing machine according to ASTM D-638 (testing speed, 50mm/min).

3. Results and discussion

The effect of flame retardant type on combustion and mechanical properties of HIPS has been investigated from 5 different flame retardants as follows: Organically modified montmorillonite (OMMT); Bisphenol A bis-(diphenylphosphate) (BDP); 9,10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide (DOPO); Magnesium Hydroxide (MH) and

Triphenyl Phosphate (TPP). The results of flame tests and mechanical properties will be later analyzed.

3.1 LOI and UL94 analysis

In flame retardant study, the flammability will be tested by UL-94 and limit oxygen index test. The results are shown in Table 1.

Sample	%LOI	UL94	Burning rate (cm/min)
HIPS	18.5	NC*	5.90 ±0.40
HIPS + OMMT 3 phr	22.5	V0	-
HIPS + MH 15 phr	21.5	NC*	2.22 ±0.23
HIPS + BDP 15 phr	22.5	V0	-
HIPS + DOPO 15 phr	22.5	V0	-
HIPS + TPP 15 phr	22.5	V0	-

*NC = not classified

Table 1. LOI, UL94 and Burning Rate of pure HIPS and HIPS with various flame retardants

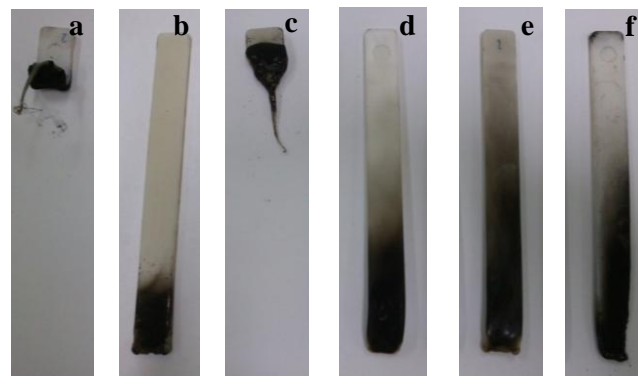


Fig.1 Photograph of sample after UL94 test (a) HIPS pure, (b) HIPS+OMMT, (c) HIPS+MH, (d) HIPS+BDP, (e) HIPS+DOPO and (f) HIPS+TPP

Virgin HIPS could be burnt quickly and has no classified rating in UL-94 test with only 18.5% of LOI. When adding flame retardant in HIPS matrix, LOI was obviously increased.

MH under heating will decompose and release water which can reduce the temperature during polymer burning, dilute produced flammability. The residue of MgO from MH burning is considered relatively high thermal stability. It will cover the surface of polymer as char layer which can insulate the product from further thermal degradation. [8, 9] The thermal stability of MgO can be substantiated by high percentage of residue at high temperature (up to 7.67%) from TGA measurement as shown in Fig. 2. However, LOI of HIPS+MH is the lowest one and there is no classified rating in UL-94 test. HIPS with MH is not qualified as a self-extinguisher. MH can only slow down HIPS burning rate to 2.22 cm/min. MH will be more effective flame retardant when the addition of its high content into polymer is incorporated. [10, 11]

Phosphate-type flame retardant: BDP, DOPO and TPP, these flame retardants can improve flame retardation properties of HIPS to achieve V-0 rating in UL-94 test. They can be self-extinguish and cause no polymer dripping effect. For all 3 components, the LOI are at 22.5%. Generally, the action of flame retardation can be both at the condensed phase and the vapor phase. And for the Phosphate-type flame retardant, it will act rather high in vapor phase with

the low content of residue as shown Fig.1. The result conforms to TGA measurement which has low residue at high temperature (Fig.2). In gaseous phase action, the vapor contains $\text{PO}_2\cdot$, $\text{PO}\cdot$ and $\text{HPO}\cdot$ which further react with $\text{H}\cdot$ and $\text{OH}\cdot$ radicals from phosphorus compound to retard burning and dilute oxygen in the air. [4, 8, 12-14] The result from UL-94 test and LOI of these phosphate compounds are considered to be similar.

The other flame retardation process can be accomplished by adding OMMT as a flame retardant which increased LOI to 22.5% with the achievement of V0 classified rating. In this study, flammability was reduced at the low content of 3 phr when comparing with other phosphorus flame retardant. The action of OMMT is begun when the sample is exposing to higher temperature. There will be organomodifier thermal decomposition and strongly protonic catalytic sites build up onto the clay surface, which can catalyze the formation of a stable char residue. Therefore accumulation of the clay on the surface of the material acts as a protective barrier that limits heat transfer into the material, volatilization of combustible degradation products and diffusion of oxygen into the material. Furthermore, nanoclay migration is enhanced by the formation of gas bubbles, initiated by the decomposition of both the quaternary ammonium organomodifiers and the polymer chains. Such gas bubbles may in fact be nucleated by the surface of the OMMT. These gas bubbles could also help in the convection of the OMMT sheets to the surface. [7, 15]

Moreover, it is found that FR: OMMT, BDP, DOPO, TPP and MH could improve the thermal stability of HIPS as seen in Fig. 2. The decomposition of HIPS is divided into two steps which are the decomposition of side chain and main chain (in 1,3 butadiene) of HIPS respectively and fully decomposition with no residue at 499 °C due to small molecule from decomposition is vaporized and fully spread out. The onset of decomposition temperature of HIPS is at 366 °C with the addition of OMMT, BDP, MH, DOPO and TPP, such temperatures are raised to 393, 376, 374, 385 and 375 °C respectively. This indicates that flame retardant will increase decomposition temperature and give higher thermal stability to HIPS.

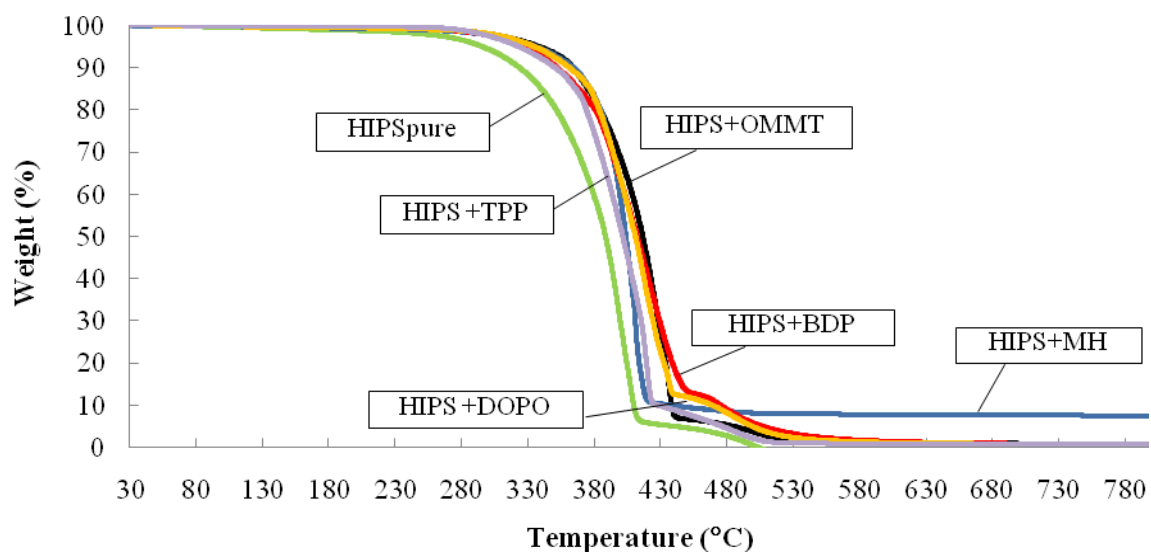


Fig.2 Thermogram of HIPS Pure and HIPS with Various Flame Retardants

3.2 Mechanical Properties

3.2.1 Impact Property

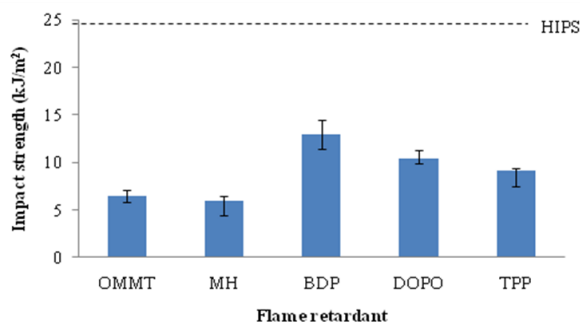


Fig.3 Impact Strength of HIPS with various flame retardants; HIPS+OMMT 3 phr, HIPS+MH 15 phr, HIPS+BDP 15 phr, HIPS+DOPO 15 phr and HIPS+TPP 15 phr respectively

Impact strength of HIPS with various flame retardants is shown in Fig.3. HIPS is derived from polystyrene to improve impact resistance. Therefore, HIPS itself has high impact strength. However, with the filler addition, impact strength of HIPS composites will be decreased due to stiffness reduction. The impact strength of HIPS composites is the lowest when adding MH and OMMT (6.5 and 6.0 kJ/m² respectively) as a flame retardant due to phase separation which led to stress transfer under impact load. For phosphate flame retardant, impact strength of HIPS will be decreased because of the containment of benzene ring in chemical structure which reduced stiffness properties in polymer but not as low as OMMT and MH addition. This is because the chemical structure of phosphate is similar to HIPS. From this study, the impact strength of each compounds are 13.00, 10.34 and 9.05 kJ/m² for BDP, DOPO and TPP respectively. Interestingly, BDP give the highest impact strength to HIPS because of a numerous –O– bond in BDP structure (Fig. 4a) which is flexible and transfer the impact force uniformly to the matrix.

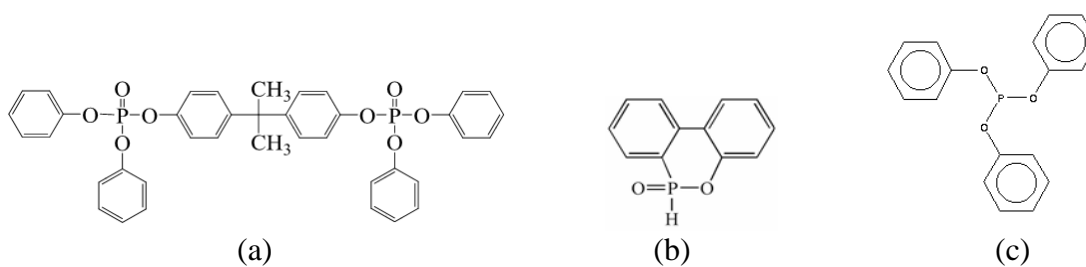


Fig.4 Chemical Structure of (a) BDP, (b) DOPO and (c)TPP

3.2.2 Tensile properties

Flame retardant addition will reduce tensile strength of HIPS. OMMT compound exhibits a slight decrease in tensile strength due to the addition of only a small amount of filler compared with other flame retardants, thus, less stress concentration in HIPS matrix. According to Fig.5, the second highest of the tensile strength is the one of HIPS with MH because of the inorganic compound of metallic hydroxide with relatively higher stiffness. And the phosphate-type flame retardant yields comparatively the lowest number of tensile strength of all HIPS compounds which illustrated less stiffness due to the –O– bond mentioned earlier.

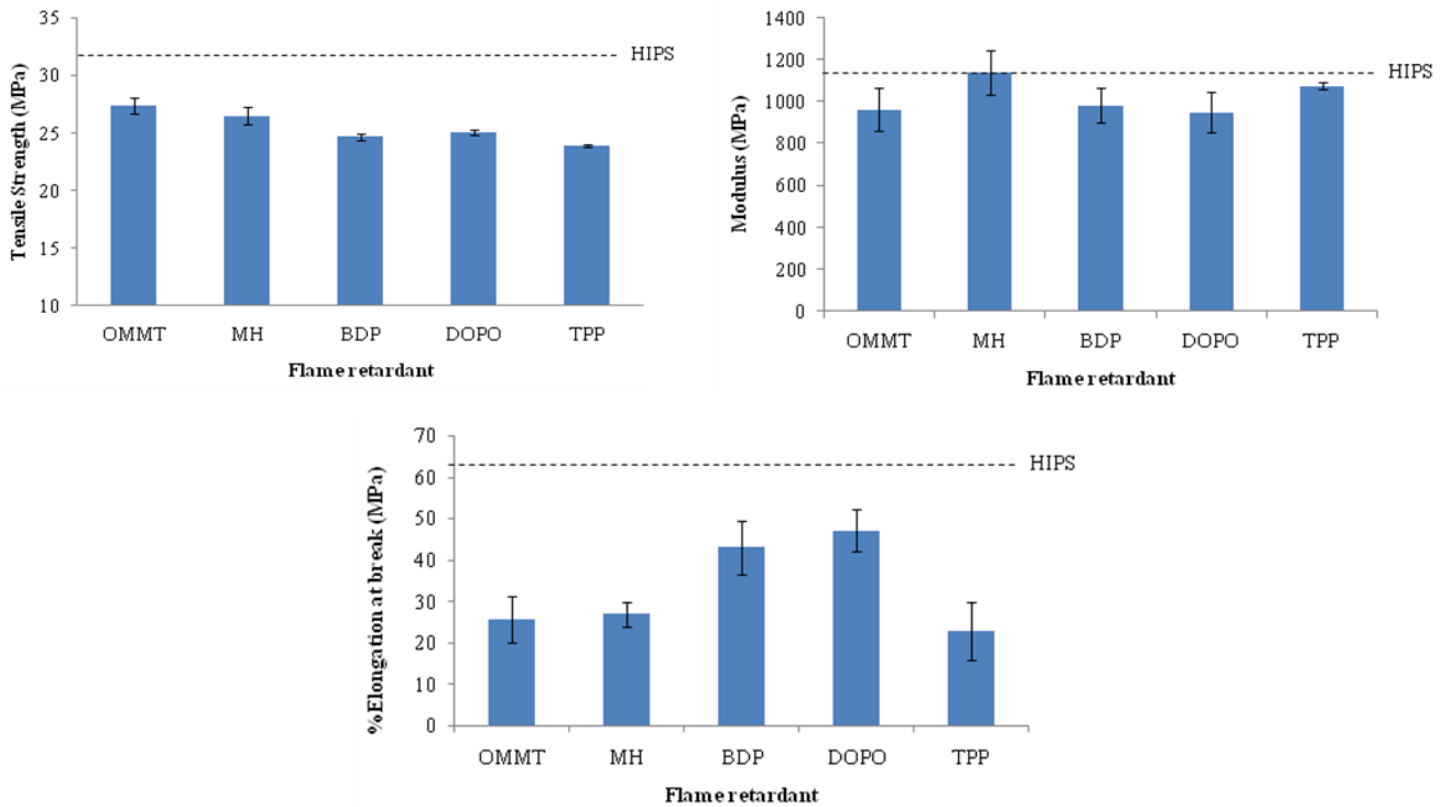


Fig.5 Tensile Strength, Tensile modulus and %Elongation at Break of HIPS with various flame retardants

In term of Young's modulus, the modulus of HIPS compound was decreased once the flame retardant was added for every type of additives except MH. Even the OMMT in a small amount was added, however, could reduce the modulus of HIPS for a certain extent. This might be the phase-separation caused by OMMT. The flexible structure of phosphate-type flame retardant compound would undoubtedly reduce the modulus once it was incorporated into the HIPS compound. As mentioned earlier, MH could be distributed well as shown in SEM micrograph in Fig.6 and thus had no impact on the modulus and retained its tensile modulus as its virgin HIPS.

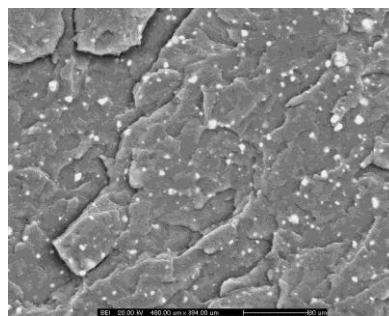


Fig. 6 SEM graph of HIPS+ MH 15 phr at 250x

Flame retardant addition would reduce the percentage elongation of HIPS because this particle would obstruct chain movement of HIPS and caused the reduction in elongation. It was also found that BDP and DOPO provided the highest percentage elongation at break to HIPS compound.

4. Conclusions

Flame retardant improvement of HIPS can be accomplished by adding OMMT, BDP, DOPO and TPP which can achieve V-0 rating in UL-94 test and increase %LOI. HIPS with each flame retardant possess relatively higher thermal stability than the virgin one with the sacrifice in mechanical properties. HIPS incorporated with BDP exhibits the highest impact strength and with moderate tensile strength.

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