

# Studies on the Effects of Various Flame Retardants on Polypropylene

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**Abstract** Polypropylene is a linear saturated hydrocarbon polymer. In this article, the impact of a typical fire retardant mixture of Ammonium Polyphosphate(APP) and Pentaerythritol(PER) on the fire retardant characteristics of polypropylene(PP) has been studied. The various impact of the fire retardant mixtures (APP-PER) was studied at different proportions of 3:1 and 4:1 on the PP. To observe the effect of the composition of mixtures of both (3:1 & 4:1) on PP was studied in the different mixing compositions (15%, 30% & 40%). In this experiment, the flame retardant(FR) was operated by intumescent method. The effect of various flame retardants on PP were studied by preparing a ternary mixtures of PP-APP-PER on Brabender mixture at 180°C for 10 min at a speed of 80rpm. The mixture was hot pressed at 180°C under 10MPa pressure for 12 min to prepare sheets of suitable thickness for analysis. The prepared sheets were subjected to the laboratory test such as, Limiting Oxygen Index(LOI) and Thermogravimetric Analysis(TGA) to find out the burning behavior and changed in the weight of a specimen respectively. The flammability test was carried out to study the flame retardancy behavior of the specimen. The degradation of PP is influenced with the increase content of phosphorous in the APP-PER mixture. LOI test indicates an improvement in flame retardancy of PP due to presence of high phosphorous content in 4:1 mixture.

**Keywords** Flame Retardants, Polypropylene, Ammonium Polyphosphate, Pentaerythritol, Limiting Oxygen Index

## 1. Introduction

Polypropylene has a wide range of application in the field of textiles. The morphological structure of polypropylene is rather complex and at least four different types of spherulite have been observed. The properties of the polymer depend on the size and types of crystal structure formed. These properties are generally influenced by the ratio of the relative rates of nucleation to the crystal growth. The ratio of these two rates can be controlled by varying the rates of cooling and by the incorporation of nucleating agents. In general, the smaller the crystal structure, the greater is the transparency and flex resistance, lesser the rigidity and heat resistance. Polypropylene is widely used in a large variety of common polymers as thermoplastic material because of its excellent mechanical properties, low density, good thermal and chemical resistance and easy processing. The polypropylene has limited use on electric and electronic materials because of their easy flammability with low limiting oxygen index which are the order of 18% [1]. In order to improve the flame retardancy of polypropylene, reinforcing agents and flame retardants are added to PP.

Commercial polymers are usually about 90%-95% isotactic. The isotactic polypropylene has low density and high softening point. Polypropylene appears to be free from environmental stress cracking resistance. The only exception seems to be with concentrated sulfuric acid, chromic acid and aqua regia. It is more susceptible to oxidation at elevated temperatures and it has higher brittle point. The importance of flame retarding thermoplastics is to increase the resistance of a material to ignition and once ignited, to reduce the rate of flame spread. The type of flame retardant and the quantity needed to meet specific objectives depend on the specific polymer. Various halogen or phosphorus [2] containing flame retardants such as metal hydroxides and oxides [3], nano-composites [4] and intumescent [5] systems are usually synergistically applied in PP composites to improve their flame retardant efficiency [6].

Additive as well as reactive flame retardants are available commercially. The addition of large quantities of flame retardants may severely degrade the properties of thermoplastic and may also present processing problems. Flame retardants (FR) that plasticize the polymer reduce thermal properties such as heat distortion temperature whereas non melting solid additives may severely degrade impact properties. To enhance the FR efficiency of intumescent flame retardants (IFRs) many synergists have been introduced into the system, including sepiolate [7], vermiculate [8], fumed silica [9], iron powder [10], metal

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oxides[11], nickel phosphates[12], zeolites[13] and mentm orillnate[14].

The adverse effect of flame retardants on the environment may be reduced by using various halogen free flame retardants and intumescent flame retardants. Polypropylene is of great importance in use because of little smoke and low toxicity during burning[15-19]. These retardants also produce very low toxic smog and anti dripping.

In this study, care has been taken to find out the effects of various flame retardants on PP as well as to meet the environmental problems. The objectives of this study are to study the impact of a typical fire retardant mixture of Ammonium Polyphosphate and Pentaerythritol (APP-PER) on the fire retardant characteristics of Polypropylene (PP). The various impact of the fire retardant mixtures (APP-PER) at different proportions (here 3:1 and 4:1) on the PP has also been studied. The composition of mixtures of both (3:1 and 4:1) fire retardant additive mixtures and PP also studied in different mixing compositions (15%, 30% and 40%) to observe the impact. The study is also meant for comparing the oxygen indices of these mixtures measured before and after addition of additives. The relative effect of fire retardant additive is being determined by adding polypropylene to it. In this process the increasing or decreasing rate of thermal oxidation value of PP was observed. A comparative study of the efficiency of fire retardant additives is carried out by using different mixture compositions and addition proportions of fire retardants so that an overview of the trend on may be made.

## 2. Experimental

Flame retardants may function by intumescence[20], polymerization[21], melt dripping[22], flame poisoning[23], charring[24, 25], cooling[26] and/or by forming protective coating[27]. In this experiment, the FR was operated by intumescence method.

## 3. Materials

Isotactic PP shows higher stability at higher temperature up to 100°C and higher stress cracking resistance. Because of its tertiary carbon atoms, PP has a lower oxidative stability. PP is one of the lightest thermoplastics because of its low density (0.9 - 0.91). A large scale production of PP uses co ordination polymerization with Ziegler-Natta catalyst. The structure of PP is given in Fig. 1.

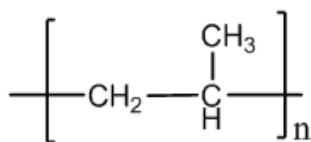


Figure 1. Structure of Poly-Propylene

Specific additives enhance the characteristics of PP or

impart the properties not normally present in PP. The three types of PP such as homopolymers, random copolymers and impact copolymers exhibit distinct properties and it is rare that one type can be interchanged with another without compromising some performance properties.

APP is a stable non volatile compound. In contact with water, APP slowly gets hydrolysed to mono-ammonium phosphate (ortho-phosphate). The hydrolysis process may be accelerated at higher temperature and prolonged exposure to water. Long chain APP starts to decompose at temperature above 300°C to Poly(phosphoric acid) and ammonia. Short chain APP begins to decompose at temperature above 150°C. APP and APP based systems are very efficient halogen free flame retardants. It is a non toxic eco-friendly material and it doesn't produce additional quantities of smoke due to the unique mechanism of intumescence. Compared to other halogen free systems, APP requires lower loading. The structure of APP is given in Fig. 2.

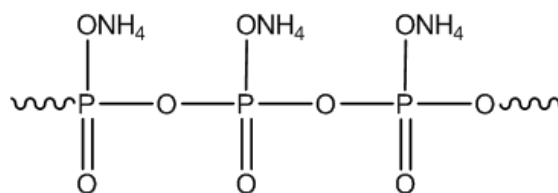


Figure 2. Structure of Ammonium Polyphosphate

PER is a white crystal powder, water soluble. It is a tetrahydric neopentyl alcohol having density 1.40g/cm<sup>3</sup>, boiling point 276 °C and melting point 260.5 °C . It is non-volatile and stable in air. Expose to high temperatures, these PER or PER based resin esters froth and swell to produce a solid, non combustible residue which serves to protect the material from fire. Halogen free pentaerythriols are environmentally friendly compounds. These are readily biodegradable and non-hazardous in water. Their low volatility and high flash point impart them excellent resistance to ignition in case of major electrical failure and transformer rapture. The structure of PER is given in Fig. 3.

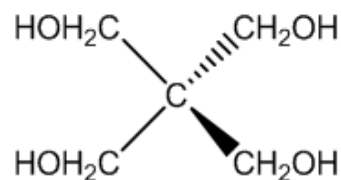


Figure 3. Structure of Pentaerythritol

## 4. Sample Preparation

The intumescent flame retardants consist of APP, PER, and PP. The ratio of APP to PER was fixed at 3:1 & 4:1 and loading of these mixtures was kept at 15, 30 and 40 wt (%) to the PP in the IFR system respectively. All composites were prepared in a Brabender mixture at 180°C for 10 min at a speed of 80 rpm. After mixing, the samples were hot pressed at 180°C under 10 MPa pressure for 12 min into sheets of

suitable thickness for analysis.

## 5. Methodology

### 5.1. Determination of Limiting Oxygen Index (LOI)

A complete assessment of the oxygen index was conducted using top surface ignition. A small test specimen was supported vertically in a mixture of oxygen and nitrogen flowing upwards through a transparent chimney. The upper end of specimen was ignited and the subsequent burning behavior of the specimen was observed to compare the period for which burning continues or the length of specimen was burnt with specified limits for each burning. By testing a series of test specimens burning in different oxygen concentration, the minimum oxygen index (the minimum concentration of oxygen) was determined by this method expressed in terms of volume percent in a mixture of oxygen and nitrogen which just support the flaming combustion of material initially  $23 \pm 2^\circ\text{C}$  under the conditions of test method. As per this procedure, LOI data of all samples were obtained at room temperature on an oxygen index instrument (Oxygen Index tester- S.A Associates, Delhi). Based on ASTM D2863-77 standard, the dimensions of all samples taken in this experiment were  $130 \times 6.5 \times 3 \text{ mm}^3$  [28].

### 5.2. Thermogravimetric Analysis

Thermo-gravimetric analysis (TGA) is a technique in which the weight change of a specimen is monitored with progressive heating. The components of the sample

decomposed at different temperatures. This leads to a series of weight loss that allow the components to be quantitatively measured. A typical high performance apparatus consists of an analytical balance supporting a platinum crucible fixed in an electric furnace was used for the experimental work.

TGA is very useful in characterizing polymers containing different levels of additives by measuring the degree of weight loss. The thermal stability of a polymer can be obtained through a kinetic analysis of the decomposition profile. TGA was performed on a TGA-1500 (Rheometric Scientific) at a heating rate of  $10^\circ\text{C min}^{-1}$ . Sample weight was kept within 5 to 10mg. The sample was examined under pure nitrogen condition at a flowing rate of  $50 \text{ ml min}^{-1}$  at temperatures ranging from 50 to  $700^\circ\text{C}$ .

## 6. Results & Discussion

The results obtained from the experimental work of limiting oxygen index and thermo gravimetric analysis of the samples are given in the Table No.1 and 2 respectively.

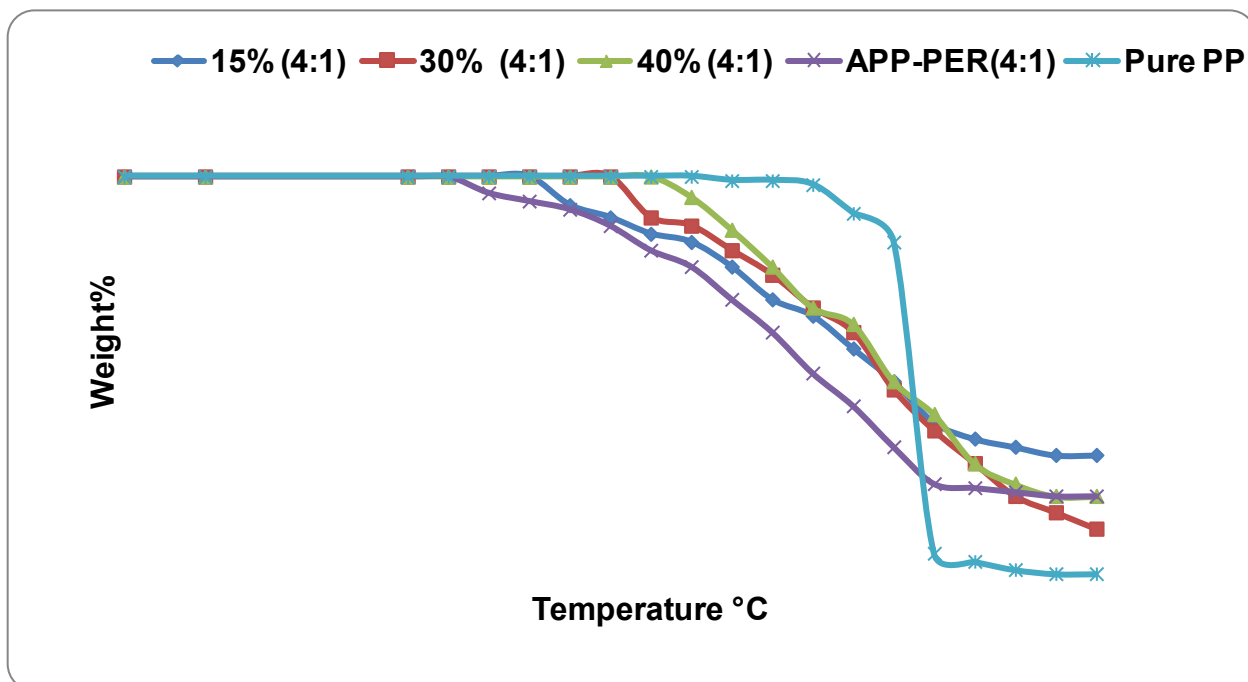
**Table 1.** Limiting Oxygen Index

Sample	LOI
PP	22
15%APP-PER(3:1)	27
30% APP-PER(3:1)	44
40% APP-PER(3:1)	65
15% APP-PER(4:1)	32
30% APP-PER(4:1)	49
40% APP-PER(4:1)	71

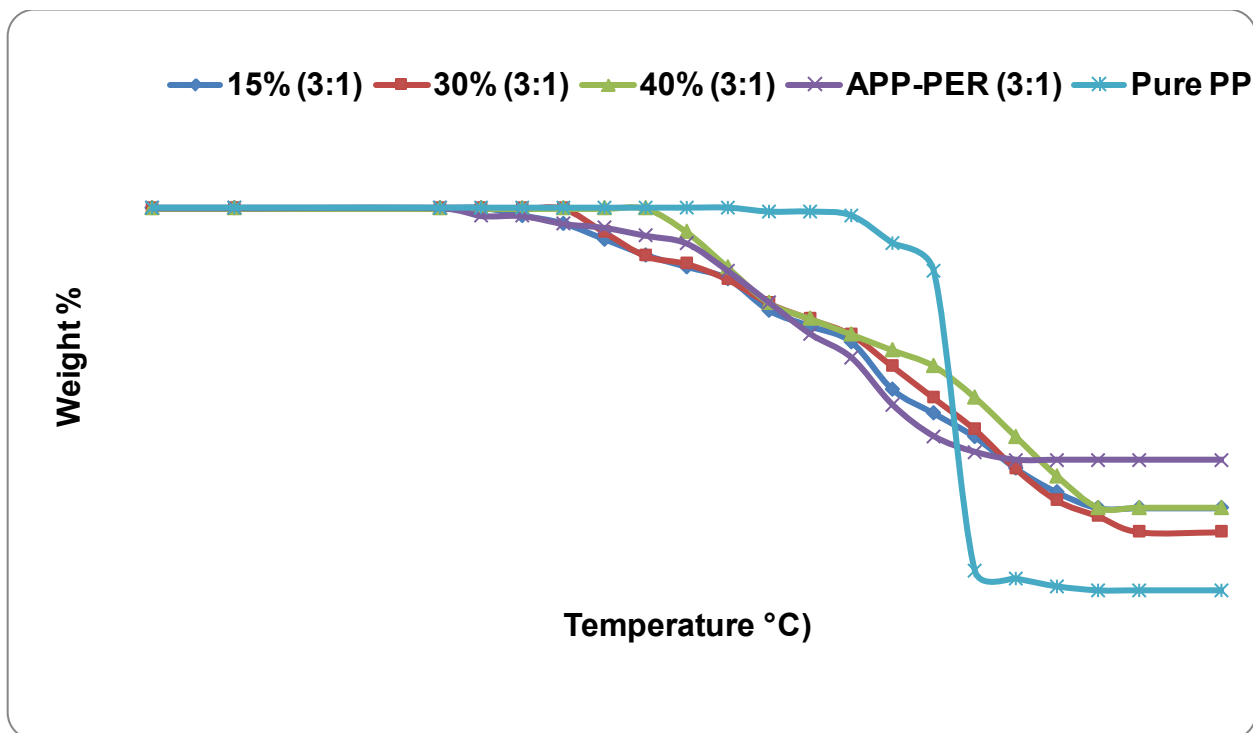
**Table 2.** TGA of PP-APP-PER(APP-PER 3:1 & 4:1 w/w) mixture with PP at different Proportions (15%,30%&40%) at different Temperatures

Temperature ( $^\circ\text{C}$ )	15 % (4:1)	30% (4:1)	40% (4:1)	APP-PER (4:1)	Pure PP	15% (3:1)	30% (3:1)	40% (3:1)	APP-PER (3:1)
0	100	100	100	100	100	100	100	100	100
50	100	100	100	100	100	100	100	100	100
175	100	100	100	100	100	100	100	100	100
200	100	100	100	100	100	100	100	100	98
225	100	100	100	96	100	98	100	100	98
250	100	100	100	94	100	96	100	100	96
275	93	100	100	92	100	92	94	100	95
300	90	100	100	88	100	88	88	100	93
325	86	90	100	82	100	85	86	94	91
350	84	88	95	78	100	82	82	85	84
375	78	82	87	70	99	74	76	76	76
400	70	76	78	62	99	70	72	72	68
425	66	68	68	52	98	66	68	68	62
450	58	62	64	44	91	54	60	64	50
475	50	48	50	34	84	48	52	60	42
500	40	38	42	25	8	42	44	52	38
525	36	30	30	24	6	34	34	42	36
550	34	22	25	23	4	28	26	32	36
575	32	18	22	22	3	24	22	24	36
600	32	14	22	22	3	24	18	24	36
650	32	14	22	22	3	24	18	24	36
700	32	14	22	22	3	24	18	24	36

The TGA curves of PP-APP-PER (4:1 and 3:1 w/w) APP-PER mixture with PP at different proportions with respect to temperature are given in the Fig 4 & 5 respectively.



**Figure 4.** TGA curves of PP-APP-PER (APP-PER 4:1 w/w) mixture with PP at different Proportions (15%, 30% & 40%) Temperatures



**Figure 5.** TGA curves of PP-APP-PER (APP-PER 3:1 w/w) mixture with PP at different Proportions (15%, 30% & 40%) Temperatures

The thermal degradation of Polypropylene (PP) indicates that it started degrading at the temperature approximately 375°C and degraded completely below 500°C. It may be due to the reason that oxygen drastically affected both the degradation mechanism and the rate of decomposition. In this work the decomposition temperature was reduced by

about 125°C. It may be due to the penetration of oxygen to some extent below the surface of PP. A typical mixture of fire retardants APP-PER in the ratio of 3:1 and 4:1 was added at different composition of percentages like 15%, 30% and 40% to the PP. The pure mixture of APP-PER in the ratio of 3:1 started degrading at the temperature about 200°C where

as mixture of APP-PER only at the ratio 4:1 started decomposing at the temperature about 225°C. It indicates that the degradation of PP is influenced to some extent with the increase content of phosphorous in the APP-PER mixture.

After the addition of APP-PER mixture (3:1 and 4:1) to the PP in the composition of 15%, it was observed that the degradation of PP-APP-PER mixture was taken place at nearly 225°C and 275°C temperature respectively. It was observed that in the case of 3:1 at 15% composition, the weight loss was more than that of 4:1 at 15% composition. It may be due to the reason that the more phosphorus content, the more is the weight loss. It is because of the formation of ammonia and water at this temperature through the reaction between APP and PER. Also at low PER-APP ratios, insertion of bicyclic PP phosphate units in the APP chain would occur, it further leads to an increase the degradation process. In entire degradation process of APP-PER mixtures, relatively large amount of non flammable volatile products ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ) are evolved as per the chemical reaction of APP and PER, given below in Fig. 6.

From the experiment, it was found that PP-APP-PER mixtures were degraded much earlier due to the presence of APP-PER in PP. In this process the evolution of the diluent gases ( $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ) may help the mixture to act as fire

retardant additives in addition to their intumescence properties.

Similarly the degradation of PP-APP-PER mixtures in both the ratio 3:1 and 4:1 at the composition percentage of 30% start degrading at 250°C and 300°C temperature respectively. It was also observed that at the composition of 40% APP-PER mixture, the degradation temperature were 300°C and 325°C respectively. These observations indicate that as the phosphorus content increases, the effective flame retardancy also increases. By increasing the temperature to about 350°C, it was found from the experiments that the total weight loss for the mixtures of 3:1 and 4:1 of both compositions (30% and 40%) was lesser significant to that of the case of 40% of both 3:1 and 4:1. It was observed that the pure PP has high degradation temperature while the mixture of APP-PER has low degradation temperature. Char formation may be increased by adding the additives which react with the degrading polymer and promote the char formation. The char formation increases the thermal stability hence reduces the flammability. When the additives are added, the degradation seems to be induced by partial charring of PP. The char formation may be increased the phosphorus content which may increase the effective flame retardancy of the PP.

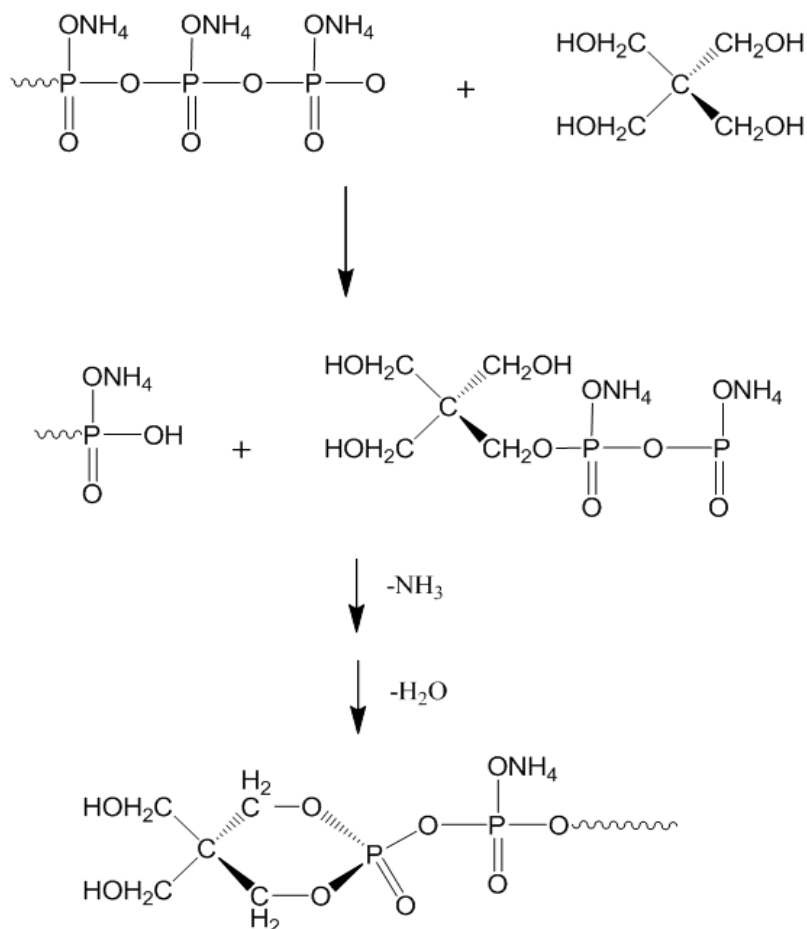


Figure 6. Chemical reaction of APP and PER

## 7. Conclusions

The thermal degradation of Polypropylene mixed with fire retardant APP-PER (4:1) has lower value than that of (PP-APP-PER) mixture(3:1). It may be concluded that the fire retardancy property of polymer increases with the increasing content of phosphorous in FR. The composition of volatile products formed by degradation of PP in presence of the additives(both 3:1 and 4:1) has little impact on the properties of the polymer. The effective flame retardancy of PP is more because of the higher phosphorous content (4:1) in the fire retardant mixture(APP-PER). It was also confirmed from the result obtained from LOI test.

As the loading percentage of additives increases, the effective flame retardancy of PP also increases but less significantly. The fire retardant concentration has been kept at optimum level. The loading percentage has not been increased beyond 40% assuming that the physical as well as chemical properties of PP will be affected adversely.

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