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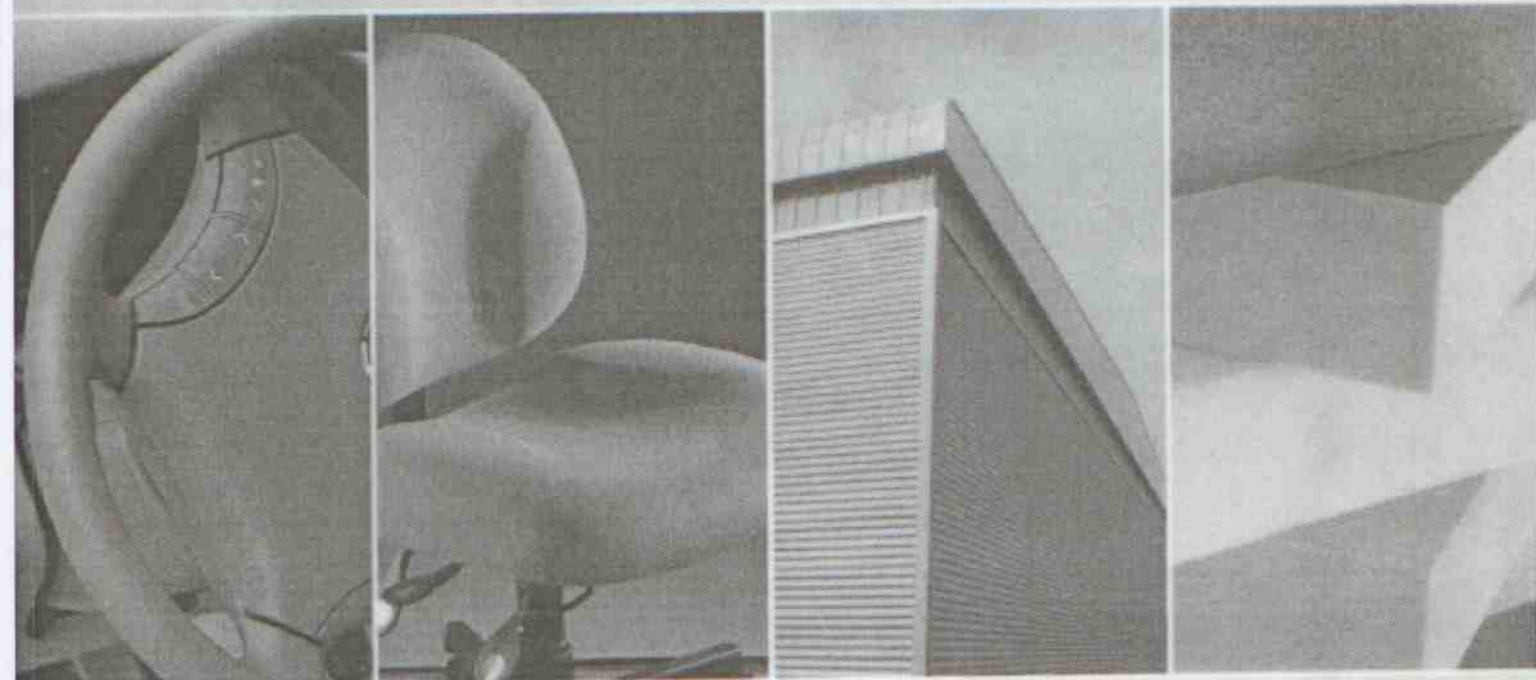


## PU TECH 2008

Polyurethane Exhibition & Conference - India

12-14 March 2008, India Expo Centre, Near Delhi, India

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## TECHNICAL SESSIONS



## **Phosphorus-Nitrogen (P-N) Based Additives Impregnated Fire Retardant Rigid Polyurethane Foam (RPUF)**

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### **ABSTRACT**

Rigid polyurethane foam (RPUF) is one of the most versatile and widely used thermal insulation material for buildings throughout the world. RPUF, being a highly cellular polymer is easily ignitable and highly flammable. On burning it undergoes decomposition and produces large quantity of vision obscuring smoke with highly toxic gases such as hydrogen cyanide and carbon monoxide etc. and thus it is important to render it flame retardant for safe use. A flame retardant composition was prepared from phosphorus-nitrogen (P-N) based additives. The flame retardancy of rigid polyurethane foam (RPUF) was studied by impregnating it with various concentrations of P-N based additives composition. Optimum impregnation time, retention and density of RPUF samples with P-N composition were also studied. The morphology, elemental analysis and thermal stability of RPUF and RPUF-P-N samples were studied with scanning electron microscopy (SEM), CHNS analyzer and energy dispersive x-rays (EDX) and, thermogravimetric analysis (TGA), derivative thermogravimetric (DTG), differential thermal analysis (DTA) respectively. The deposition of P-N on the cell walls and surfaces was exhibited by decreased cell size from 357 to 285  $\mu$ m. CHNS and EDX studies show the introduction of phosphorus and nitrogen into the RPUF-P-N samples. The degradation of RPUF and RPUF-P-N samples was occurred through two and three stages in nitrogen and air respectively. RPUF-P-N samples are decomposed comparatively at lower temperature than RPUF which is resulted into large amount of high temperature stable char residue. This char residue acts as insulating blanket and protects RPUF-P-N from fire. Fire performance of RPUF and RPUF-P-N samples were investigated with BS: 4735. RPUF-P-N samples demonstrate reduced extent burnt from 125 - 27mm, burning rate 2.23 to 0.44 mm/s and percent mass loss (PML) from 100 to 8.82%.

### **INTRODUCTION**

The worldwide demand of polyurethane foams is estimated about 5% of total world consumption of plastics. Flexible polyurethane foam is produced in large volume (48%) and finds its greater uses in mattresses and furniture cushioning. On the other hand rigid polyurethane foam is produced in lower volume (28%) and finds applications in transportation, carpet underlay, refrigeration technology and appliances, building construction industry, automotive industry, packaging and sporting goods.<sup>1-2</sup> The excellent thermal insulation properties of rigid polyurethane foam (a mere 2 inch thick foam equivalent to 3 inch polystyrene, 3.5 inch mineral wool, 4 inch cork, 6 inch glass fiber, 11 inch wood and 30 inch cemented concrete block) makes it a versatile and very important material than the rest of the insulation materials.<sup>1</sup> Rigid polyurethane foams (RPUFs) are the reaction products of high functional 4, 4' diphenylmethane diisocyanate (MDI) and low molecular weight polyether polyol. RPUFs have an extremely versatile range of properties and applications. Some of the important engineering applications are building construction industry, domestic and commercial refrigeration, transportation, automotive industry, packaging, furniture components and decorative paneling, due to their superior heat insulation value resulted from closed cell structure.<sup>1-2</sup> However, RPUFs have low thermal stability and high flammability, primarily due to the presence of biuret, allophanate, urethane and urea groups into their structure. Biuret and allophanate are the most thermally unstable groups in the RPUF backbone, and on exposure to fire immediately





decompose to diisocyanate, urea and urethane precursors. These precursors are again thermally unstable. During RPUF burning diisocyanate converts into yellow smoke containing HCN, and rest of the other groups convert to white smoke containing CO<sup>2</sup> and CO. HCN and CO are the prominent toxicant gases which on inhalation lead to death.<sup>3-6</sup>

Various fire retardants such as phosphorus - halogen mixture, ammonium polyphosphate (APP) and organo-phosphorus compounds either alone or in combination with nitrogen or silicone have been used to impart fire retardancy to RPUFs.<sup>7-9</sup> These compounds may be incorporated into the foam formulation as reactive or non-reactive additives in the form of phosphorus, nitrogen and halogen elements. Modesti et al. were recently reported the successful incorporation of various combinations of halogen free fire retardants such as APP with melamine, expandable graphite with triethyl phosphate and red phosphorus, and expanded graphite with melamine into the RPUF formulations.<sup>10-13</sup> As phosphorus and other halogen free fire retardants containing RPUFs give off non-toxic combustion products, thus they are preferred over halogen containing fire retardants.<sup>14-15</sup> Bromine and chlorine containing RPUFs on exposure to fire produce corrosive smoke of high toxicity. Organic phosphates do not cause any of these problems. The fire retardant activity of phosphorus compound starts in condensed phase. On exposure to heat, phosphorus compound decomposes at lower temperature than polyurethane foams to produce phosphoric or polyphosphoric acids. These acids catalyse the char formation in the condensed phase. This phosphorus rich char prevents heat transfer by reducing the production of combustible gases.<sup>16-17</sup> Grassie et al. reported that phosphoric acid reacts very efficiently with carbodiimide formed by the condensation of the isocyanate released on the thermolysis of polyurethane foams. Phosphoric acid - carbodiimide reaction leads to cross linking which resulted into carbonaceous char formation. This carbonaceous char prevents the heat penetration into the foam surface.<sup>18</sup>

The main objective of this study is the preparation of phosphorus - nitrogen additives based composition and to investigate the effect on the fire retardancy of rigid polyurethane foam impregnated with P-N composition. Earlier such fire retardant compositions have been studied in cellulosic paper and wood,<sup>19</sup> but never in rigid polyurethane foams to the best of authors knowledge. Rigid polyurethane foam (RPUF) impregnated with P-N composition was prepared in our own laboratory and the results are reported.<sup>20</sup> RPUF samples of similar density were impregnated with different concentrations of P-N composition. The density of RPUF samples impregnated with P-N was measured as per ASTM D1622. Morphological characteristics, elemental analysis and thermal behaviour properties in nitrogen and air atmosphere of conventional and P-N composition impregnated RPUF samples were studied with scanning electron microscopy (SEM), CHNS analyzer and energy dispersive x-rays (EDX) and, thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) differential thermal analysis (DTA) respectively. The flammability characteristics were evaluated with BS: 4735.

## EXPERIMENTAL

### Materials

Materials and chemical reagents are indigenously available and were used as they received. Distilled water used was generated in the laboratory. Rigid polyurethane foam (49.19 kg/m<sup>3</sup>) samples used for impregnation were also prepared in the laboratory.

### Preparation of P-N additives Composition

An aldehyde solution mixed with distilled water was charged in a 1000 ml three-neck round bottom flask equipped with thermometer, stirrer and reflux condenser. The medium of the solution was adjusted to alkaline by adding a few drops of an alkali solution. The solution was then heated over a water bath until it attains the temperature of 80 - 90°C. A mixture of nitrogen additives was then added incrementally with constant stirring over 20 minutes. Upon the completion of the addition, the reaction mixture was allowed to reflux for 10 minutes. The resulting solution was cooled to ambient temperature by putting the flask under cold-water stream. Phosphorus additive was then added slowly with constant stirring. During the addition of phosphorus additive, the whole assembly was continuously kept under cold-water stream to avoid the heat up of flask due to the heat generated by the reaction of





phosphorus additive and mixture solution. The final product was a colourless viscous liquid mixture of phosphorus-nitrogen additives. This viscous mixture was designated as P-N additives. The basic formulation used for the P-N additives preparation is presented in Table 1.

**Table 1:** Basic Chemical Formulation of P-N Additives Composition

Chemical	Quantity per mole
Phosphorus additive	1.0
Nitrogen additive-1	0.25
Nitrogen additive-2	1.0
Aldehyde solution	3.0
Water	8.0

### SAMPLE PREPARATION

Conventional RPUF samples of 49.19-kg/m<sup>3</sup> densities were used for impregnation with P-N additives composition. P-N additives composition concentration, impregnation time, retention and density are considered to be the most important parameters during the preparation of RPUF samples. P-N additives is water based composition, thus its various concentrations ranging from 10-100% were prepared by mixing it with water. Optimum impregnation is the time at which RPUF samples retain the maximum quantity of P-N additives with optimum time period. Optimum impregnation time was investigated by impregnating the RPUF samples with 100% P-N additives solution concentration from 10-60 min. with an increment of 10 min. at the ambient conditions. Retention is the quantity of P-N additives solution concentration absorbed by the RPUF sample and subsequently retained in it. Retention of RPUF samples was investigated by impregnating the 30 number of samples for optimum time with 10-100% P-N additives concentrations with an increment of 10%. The effects of P-N additives concentration and impregnation time on retention were studied by impregnating the 180 numbers of RPUF samples into the P-N additives solution concentration ranging from 10-100% and every three samples were removed from the solution at an interval of 10 minutes. The effect on the density of RPUF samples was observed by impregnating the samples for optimum time with 10-100% P-N additives concentrations with an increment of 10%. After complete impregnation, RPUF samples were removed from their respective P-N additives solution concentration and allowed to dry for 24 hours at room temperature. P-N additives solution concentration and optimum impregnation time of RPUF samples (RPUF-P-N) are shown in Table 2. In the sample code, P-N denotes the phosphorus-nitrogen additives composition concentrations used for impregnation. RPUF samples impregnated with P-N additives are shown in Figure 1 (a).

**Table 2:** Rigid Polyurethane Foam samples (RPUF-P-N)<sup>a</sup> impregnated with Phosphorus – Nitrogen additives based composition

Sample codes (RPUF-P-N)	P-N Concentration (%)	Water (%)	Impregnation time (min)
RPUF-0.0	0.0	0.0	0.0
RPUF-P-N	10	90	20
RPUF-P-N	20	80	20
RPUF-P-N	30	70	20
RPUF-P-N	40	60	20
RPUF-P-N	50	50	20
RPUF-P-N	60	40	20
RPUF-P-N	70	30	20
RPUF-P-N	80	20	20
RPUF-P-N	90	10	20
RPUF-P-N	100	0.0	20

<sup>a</sup>P-N denotes phosphorus-nitrogen additives composition



Conventional RPUF and RPUF-P-N samples with maximum retention were prepared for scanning electron microscopy (SEM), CHNS analyzer and EDX and, thermal analysis (TGA/DTG/DTA). The flammability characteristics of conventional RPUF and RPUF-P-N samples of dimensions 150 50 13 mm were investigated by impregnating the three samples with each P-N additives composition concentrations ranging from 0-100% with an increment of 10%. After impregnation the RPUF samples were removed from the solution and dried for 24 hours at room temperature. Dried RPUF samples were marked across their width by a line (gauge mark) 25 mm from one end.

## MEASUREMENTS

P-N additives impregnation extent to the RPUF samples mainly depends upon the concentration, impregnation time and retention. These three parameters are linked to each other in which impregnation time depends upon the maximum retention, and retention depends on both concentration and impregnation time. Optimum impregnation time was measured on the basis of maximum P-N additives retention attained by the RPUF samples with respect to time. Further, optimum impregnation time on the basis of maximum retention of every three RPUF-P-N samples was calculated and averaged. Retention on each P-N additives concentrations were also calculated and averaged. The density of conventional RPUF and RPUF-P-N samples was measured according to ASTM D1622. The size (length width thickness) of the specimen was 30x30x30 mm respectively. Conventional RPUF and RPUF-P-N specimens were conditioned at 25°C and 55% relative humidity for 48 hours prior to their density measurement. The density of five specimens per sample were measured and averaged.

The morphology of conventional RPUF and RPUF-P-N samples was observed with LEO (438 VP, UK) scanning electron microscopy (SEM). The samples were cryogenically fractured and gold coated to render them conductive prior putting under scanning observation. During scanning 15 KV accelerating voltage was used. The SEM was used to observe the P-N additives deposition on the cell walls, surfaces and the difference in the shape and size of the cells between conventional RPUF and RPUF-P-N samples. To define the cell size, measured cell sizes were averaged except the sizes for the largest and smallest cells. Elemental analysis of conventional RPUF and RPUF-P-N samples was carried out with CHNS analyzer (Elementar Andysensysteme GmbH VarioEL III, Germany) and EDX. RPUF and RPUF-P-N samples powder were mixed with oxidising agent and dropped into the CHNS chamber at about 7000C. The same samples which were used for morphological observation were also used for the EDX study. The main purpose was to detect the qualitative and quantitative presence of elements introduced into the structure of RPUF samples by the P-N additives impregnation. Thermal properties of conventional RPUF and RPUF-P-N samples were measured on a Pyris Diamond Perkin-Elmer (USA). The samples were crushed into power. Platinum pan was used to place the samples powder inside the heating chamber. The samples were heated up to 1000°C at a rate of 10°C/min. in nitrogen and air atmosphere. After complete heating of the samples TGA, DTG and DTA curves obtained were taken for analysis.

The flammability characteristics of conventional RPUF and RPUF-P-N samples were evaluated according to BS: 4735. The specimens were weighed before placing horizontally on support gauge inside the non-combustible chamber. The farthest end away from gauge mark of the specimen was exposed for 60s to 10 mm diameter wing top fitted LPG burner of 38 mm non-luminous flame height. Exposed RPUF-P-N samples are shown in Figure 1 (b). After complete fire exposure extent burnt, burning rate, percent mass loss (PML) and extinction time of three specimens per sample were measured and averaged for analysis.



Figure 1 Photographs of P-N impregnated RPUF samples (RPUF-P-N): (a) before flammability test and (b) after flammability test



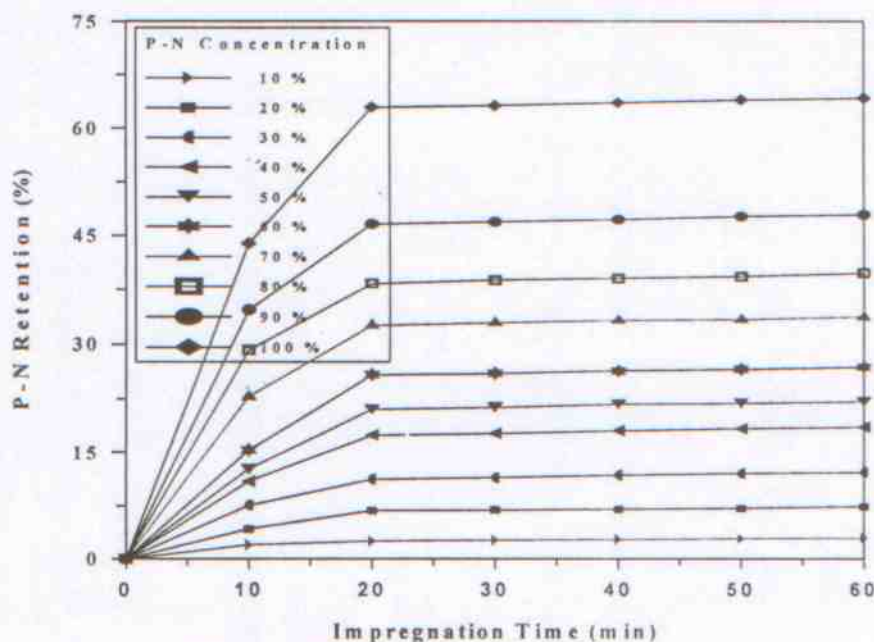
## RESULTS AND DISCUSSION

### P-N Additives Composition

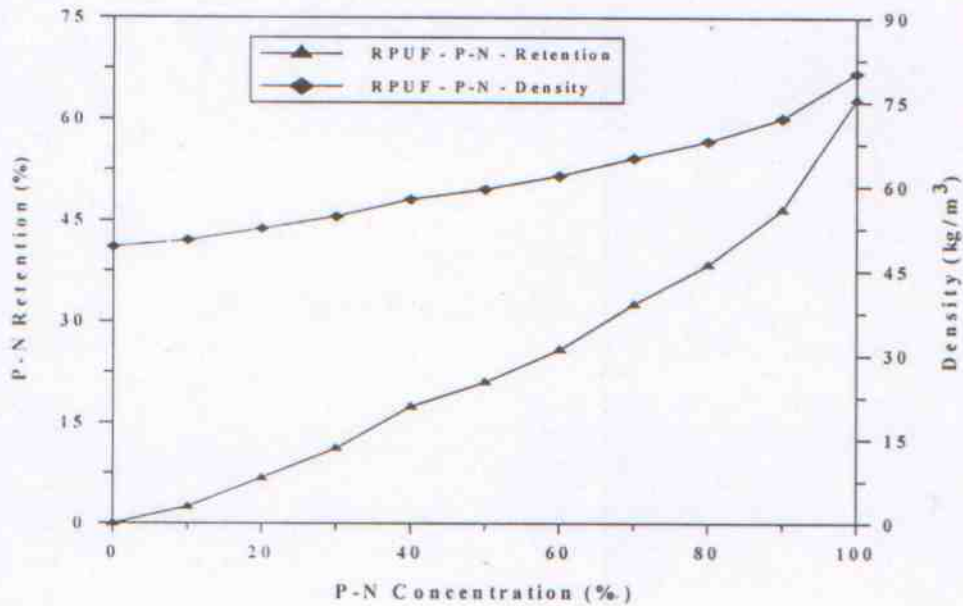
Chemical reactions involved in the preparation of P-N additives composition were already studied. It was found that one mole of nitrogen additive in alkaline medium reacts with one mole of aldehyde to form monomethylol product. Similarly to nitrogen additive-1, nitrogen additive-2 in alkaline medium reacts with aldehyde to yield monomethylolated product. When the amount of aldehyde is increased to two moles, the dimethylolated product is formed. The rate of dimethylolated product formation is very slow at room temperature. When the temperature is raised in the range of 80 - 90°C, the end product was dimethylol and no monomethylol product was formed. Thus the major intermediates in the P-N additives composition are N, N'-dimethylolated nitrogen additive-1 and N, N'-dimethylolated nitrogen additive-2. These dimethylolated products react with phosphorus additive to give 6-membered ring compound which acts as flame retardant by polymerization.<sup>19</sup>

### Concentration, Impregnation, Retention and Density

The add-on of phosphorus-nitrogen (P-N) additives composition to the RPUF samples was mainly measured from P-N concentration, impregnation time and retention. Results presented in Figure 2 show that the retention of RPUF samples was ranged from 1.98 to 64.29% when they were impregnated with 10 to 100% P-N additives concentration for 10 to 60 min. respectively. After 20 min. impregnation the retention of RPUF samples were ranged from 1.98 to 62.98% with 10 to 100% P-N additives concentration respectively, and further up to 60 min. impregnation only 1.09% average increase in the retention was observed. This may be possible due to the fact that the vacant cell space was fully occupied by P-N additive composition after 20 min. of impregnation, and no enough space was left for further impregnation at the same rate. Thus after 20 min. and up to 60 min., no appreciable increase in the retention was observed. Therefore, 20 min. is considered as the optimum impregnation time of RPUF samples. The retention and density of conventional and RPUF samples impregnated for optimum time are shown in Figure 3. As shown in Figure 3, the density increases as the retention of RPUF-P-N samples increases. When retention of RPUF samples increases from 2.49 to 62.98%, the density increases from 50.42 to 80.17 kg/m<sup>3</sup> respectively. Thus the impregnation of RPUF samples with P-N additives composition increases their densities up to 62.98%.



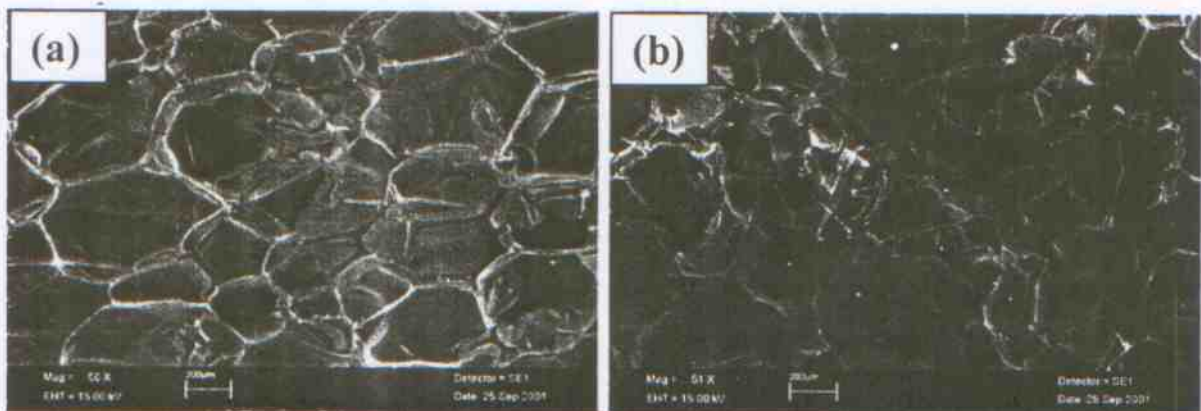
**Figure 2.** Effect of P-N concentration and impregnation time on retention of RPUF Samples (RPUF-P-N)



**Figure 3** Effect of P-N concentration on the retention and density of RPUF samples (RPUF-P-N)

### MORPHOLOGY

The cross-sectional surfaces of RPUF and RPUF-P-N samples were observed at the similar magnification under SEM. Micrographs of the RPUF and RPUF-P-N samples are shown in Figure 4 (a,b). As shown in Figure 4 (a), RPUF sample has the polyhedral and spherical cell structure of 357  $\mu\text{m}$  average cell size. Figure 4 (b) shows the deposition of P-N additives on the cell surfaces in addition to the polyhedral and spherical cell structure of RPUF. The average cell size of RPUF-P-N sample was reduced to 285  $\mu\text{m}$ . This suggests that the decrease in the cell size may be due to the deposition of P-N additives on the cell walls also. The P-N additives deposition on the RPUF skeleton is further confirmed by the fact that polyurethane phase is optically transparent.<sup>21</sup> Thus P-N additives were deposited on the cell surfaces and walls of impregnated RPUF sample.



**Figure 4** Scanning electron micrographs of RPUF samples: (a) conventional RPUF and (b) RPUF-P-N impregnated





## ELEMENTAL ANALYSIS

The elemental analysis results of the RPUF and RPUF-P-N samples obtained with CHNS analyser and EDX are compiled in Table 3 which shows the presence of various elements. The elements which are present in the minor quantities are not given in the table. Conventional RPUF shows the presence of Carbon, oxygen, hydrogen and nitrogen which are part of the backbone and thus, appear in the higher ratio. Chlorine and silicone are present due to the methylene chloride and polysiloxane ether as physical blowing agent and surfactant respectively into the RPUF formulation. Minute quantities of bromine and magnesium were also found to be present which appear due to the impurities in the raw materials. RPUF-P-N exhibits the presence of phosphorus and increased percentage of nitrogen from 5.05 to 12.51 in addition to the elements which are part of the RPUF backbone. Thus the introduction of phosphorus and enhanced percentage of nitrogen show that RPUF is properly impregnated with P-N additives composition.

**Table 3:** Elemental analysis of Conventional and P-N additives impregnated RPUF samples

RPUF sample codes	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)	Phosphorus (%)
RPUF-C <sup>a</sup>	55.15	5.67	34.14	5.05	-
RPUF-P-N <sup>b</sup>	43.74	5.62	21.48	12.51	16.65

<sup>a</sup>Conventional RPUF

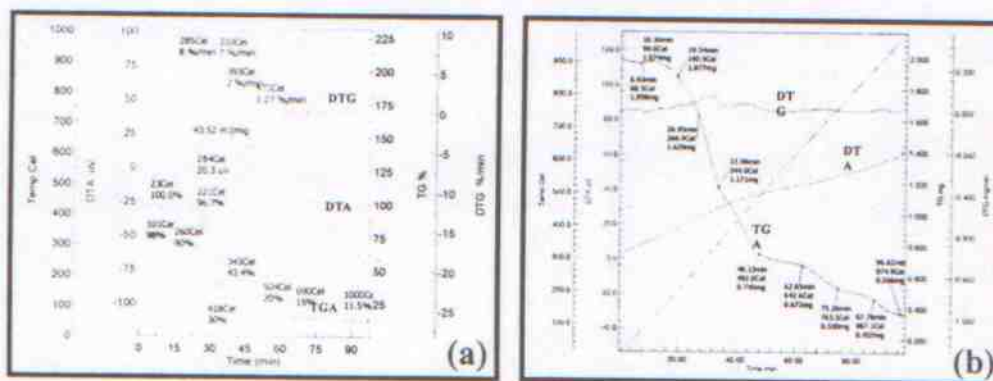
<sup>b</sup>Phosphorus-nitrogen additives impregnated RPUF

## THERMAL ANALYSIS

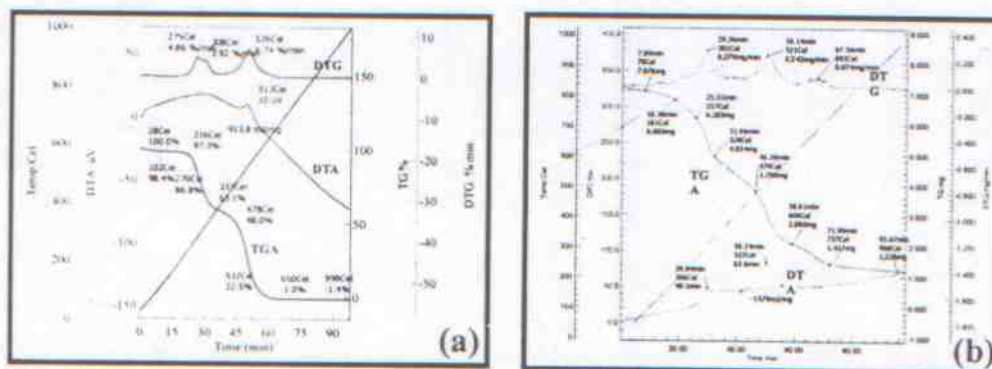
TGA/DTG/DTA profiles for conventional RPUF and RPUF-P-N samples in nitrogen and air atmosphere are shown in Figure 5 (a,b) and Figure 6 (a,b) respectively. The data of the TGA/DTG/DTA investigations are summarized in Table 4. DTG curves of RPUF and RPUF-P-N decomposition in nitrogen show only two weight loss stages, while the DTG curves in air indicate that three main weight loss stages occur during degradation. It suggests that RPUF and RPUF-P-N samples degrade through same process and degradation mechanism in air is much more complex than that in nitrogen.<sup>4,22</sup> In nitrogen atmosphere, RPUF sample does not show distinct weight loss until the temperature rises to 225°C, whereas, the degradation of RPUF-P-N begins at 180°C. During first stage, the rate of weight loss of RPUF begins to increase gradually to a maximum between 285-310°C through two successive decomposition processes. RPUF-P-N begins to degrade between 180 - 340°C with a maximum weight loss at 270°C in step first. RPUF shows minimum weight loss during pyrolysis (second stage) after the sample is heated above 500°C which leads to 12% char residue at 900°C. The degradation of RPUF-P-N starts between 400 - 520°C at maximum rate of weight loss and leads to 38 % char residue at 520°C during second step. This char residue reduces to 23% as temperature rises to 900°C. It shows that RPUF-P-N produces more quantity of char residue than conventional RPUF. The pyrolysis limits the development of volatile compounds which allows more quantity of black char residue at higher temperature. This black residue may contains carbon, and condensed aromatic contents, because biuret, allophanate, urea, urethane and disubstituted urea are the thermally weakest links in the polyurethane network.<sup>4,23</sup> Based on the TGA/DTG/DTA traces, it can be seen that decomposition of RPUF-P-N begins at lower temperature than conventional RPUF. This suggests that RPUF and P-N react first. The lower initial thermal decomposition temperature and correspondingly higher amount of stable char yield may indicate that P-N is an effective fire retardant composition. Wang et al. reported that all the phosphorus containing polyurethanes degrade at low temperatures due to the cleavage of the P-O-C bonds and hydroxyl groups which resulted into considerable amount of high temperature stable char residue.<sup>24</sup> The stable char residue provides the barrier effect to the polymer surface by reducing the heat, oxygen fluxes and rate of weight loss at higher temperature and consequently increases the flame retardancy of the polymer.<sup>11</sup>



In air atmosphere, RPUF shows three weight loss stages at the temperature regions 216-337°C, 350-478°C and 480-650°C which are consistent with the previous studies conducted and reported in the literature.<sup>3-4,9,25</sup> RPUF-P-N also degrades through three distinct weight loss stages, however, DTG analysis indicates that its initial thermal decomposition start at 160°C. RPUF exhibits minimum weight loss in first and second stages which appears to increase gradually between 480-650°C with a maximum at about 526°C during third stage. The third stage, which has 0% char residue at 900°C, appears to be thermo-oxidative in nature since it does not exist in nitrogen atmosphere.<sup>4,6,22</sup> Thus, maximum weight loss occurs in third stage is due to combustion. During combustion oxygen reacts with carbon of charred residue to convert it into volatile carbon dioxide resulting into no residue was left behind. RPUF-P-N sample degrades through single process with maximum rate of weight loss (3.22%/min) at 301°C visible on DTG peak in first stage. During second stage RPUF-P-N sample degrades exothermically at 521°C. Third steps are from the combustion which leads to 18% high temperature char residues at 900°C. The increased char residue quantity may be due to the phosphorus-nitrogen additives. The presence of phosphorus-nitrogen additives into the RPUF-P-N affects its thermal decomposition in several ways such as decreasing initial thermal decomposition temperature, attaining the maximum decomposition temperature in the early stage of degradation and degradation through single exothermic decomposition process which leads to the formation of large quantity of char residue stable at high temperature. The decomposition of RPUF-P-N at lower temperature increases the rate of maximum weight loss which resulted into maximum formation and stabilization of char residue. Lowered initial thermal decomposition temperature, maximum decomposition temperature during first step and large quantity of stable char residue in RPUF-P-N sample is very interesting in terms of fire retardancy. Phosphorus additive reacts with RPUF in the condensed phase and lowers its initial thermal decomposition temperature. Consequently, due to the decomposition at lower temperature the large quantity of stable char residue is formed in the early stage of degradation which increases the fire retardancy of foam.<sup>9</sup>



**Figure 5** Thermograms of RPUF samples in nitrogen atmosphere: (a) conventional RPUF and (b) RPUF-P-N impregnated



**Figure 6** Thermograms of RPUF samples in air atmosphere: (a) conventional RPUF and (b) RPUF-P-N impregnated





**Table 4:** Thermal behaviour and thermal stability of Conventional and P-N additives impregnated RPUF samples in nitrogen and air atmosphere

Sample codes	A/N	T <sub>on</sub> (°C)	T <sub>1max</sub> (°C)	R <sub>1max</sub> (%/min)	T <sub>2max</sub> (°C)	R <sub>2max</sub> (%/min)	T <sub>3max</sub> (°C)	R <sub>3max</sub> (%/min)	Y <sub>c</sub> (%)
RPUF <sup>a</sup>	N <sub>2</sub>	221	285	8.00	393	2.00	-	-	12
	Air	216	275	4.86	308	3.92	526	6.74	00
RPUF-P-N <sup>b</sup>	N <sub>2</sub>	180	270	1.97	520	1.52	-	-	23
	Air	160	301	3.22	521	1.93	693	1.46	18

<sup>a</sup>Conventional RPUF

<sup>b</sup>Phosphorus-nitrogen additives impregnated RPUF

A/N denotes the air and nitrogen atmosphere

T<sub>on</sub> denotes on-set degradation temperature

T<sub>1max</sub>, T<sub>2max</sub> and T<sub>3max</sub> denotes maximum degradation temperatures in first, second and third stage respectively

R<sub>1max</sub>, R<sub>2max</sub> and R<sub>3max</sub> denotes maximum rate of degradation in stage first, second and third stage respectively

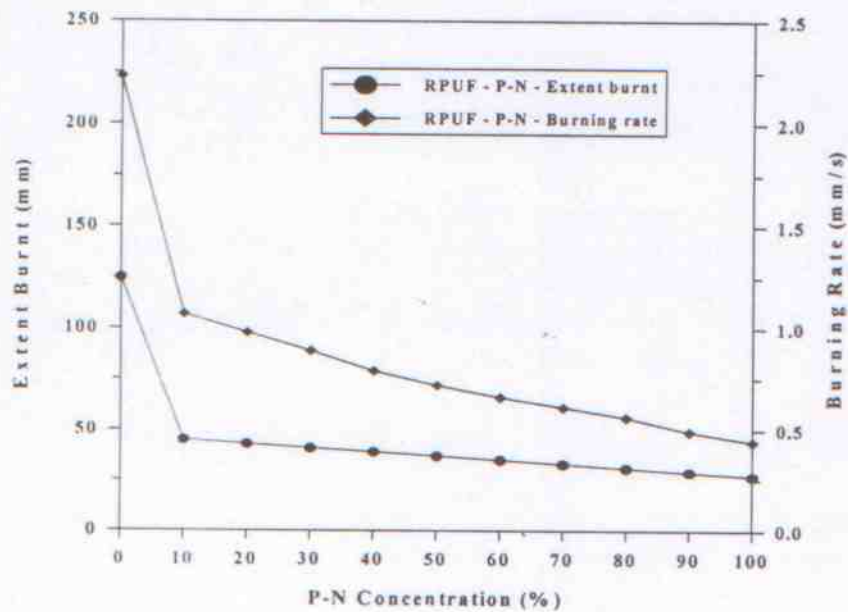
Y<sub>c</sub> denotes the char yield at 900°C.

## FIRE BEHAVIOUR

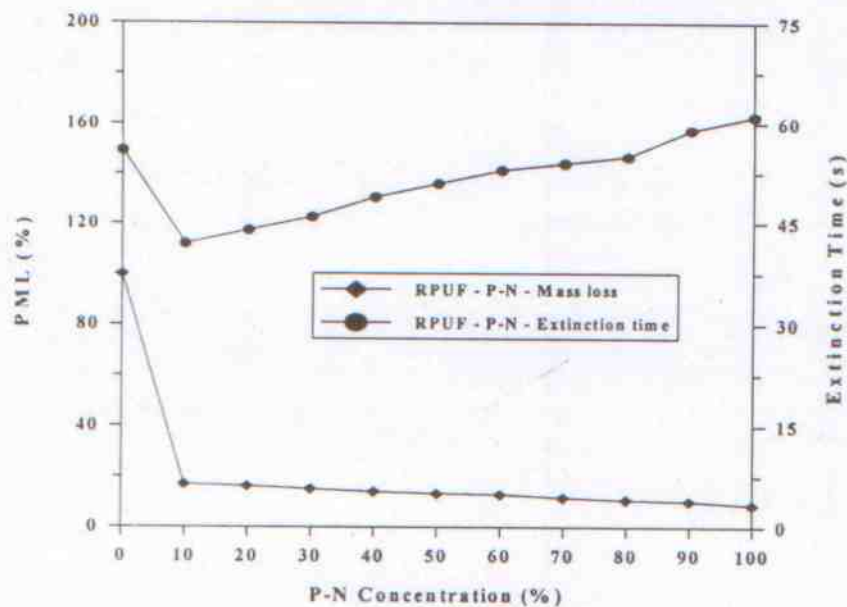
Fire performance of RPUF and RPUF-P-N samples and their comparison is mainly measured from extent burnt, burning rate, percent mass loss (PML) and extinction time obtained during the fire test. All these parameters are expressed in terms of average values. The variations of extent burnt and burning rate, PML and extinction time of RPUF and RPUF-P-N samples with respect to P-N concentrations are shown in Figures 7 and 8 respectively. Figure 7 presents the results as expected with an increasing concentration of P-N from 0 to 100%, the extent burnt and burning rate were decreased from 125 to 27 mm and 2.23 to 0.44 mm/s respectively. However, exponential difference was observed between RPUF and RPUF samples impregnated with minimum (10%) P-N concentration in their extent burnt and burning rate which were 125 mm, 2.23 mm/s and 45 mm, 1.07 mm/s respectively. The rates of decrease of extent burnt and burning rate are almost linear with the increase of P-N concentration. However, when P-N concentration increases over 90% up to 100%, there is an increase of 16.39% in the retention of RPUF-P-N, whereas, extent burnt and burning rate are decreased only by 4 mm and 0.05 mm/s respectively. Thus there is no appreciable decrease in the rate of extent burnt and burning rate, at the increasing rate of P-N concentration. As shown in Figure 8, the increasing concentration of P-N from 0 to 100% reduces the PML from 100 to 8.82%, but extinction time increases slightly from 56s to 60s respectively. RPUF and RPUF samples impregnated with minimum (10%) P-N concentration show great difference in their PML and extinction time which are 100%, 56s and 16.92%, 40s respectively. The rate of PML reduction is almost linear to 90% P-N concentration and above this PML reduces slightly as the concentration increases to 100%. RPUF samples in flammability test are consumed up to gauge mark (125 mm) in 56s. For comparison, 56s is considered as extinction time of RPUF. The extinction time of RPUF sample reduces to 42s with minimum P-N concentration, however, increases to 61s with maximum concentration. This slightly different flame extinction behaviour of RPUF-P-N samples can be explained by considering the fire retardant action of phosphorus-nitrogen additive. During flammability test the presence of phosphorus-nitrogen additive accelerates the



decomposition of foam at lower temperature which leads to an increase in the amount of high temperature stable char residue.<sup>7,9</sup> Flame extinction time is increased slightly with the increase of P-N concentration and the combined effect of these two resulted into the formation of large amount of stable char residue. The stabilized char residue acts as protective thermal barrier which does not allow further flame spread. This may leads to reduced burning rate which resulted into enhanced flame retardancy. Thus depending upon the decrease 24.8% in extent burnt, 21.9% in burning rate and 89.7% in PML and, 46.59% increase in the density of RPUF-P-N samples, P-N additives concentration of 90% can be considered as optimum.



**Figure 7** Effect of P-N concentration on extent burnt and burning rate of conventional and P-N impregnated RPUF samples



**Figure 8** Effect of P-N concentration on PML and extinction time of conventional and P-N impregnated RPUF samples





## CONCLUSIONS

In order to understand the effect of P-N composition on the structure, thermal stability, flammability characteristics and smoke density of rigid polyurethane foam (RPUF), large number of RPUF samples impregnated with various concentrations of P-N were investigated using scanning electron microscopy (SEM), CHNS analyzer and energy dispersive x-rays (EDX), thermogravimetric analysis (TGA), derivative thermogravimetric (DTG), differential thermal analysis (DTA), horizontal flammability as per BS: 4735, oxygen index as per ASTM D2863 and smoke density according to ASTM E662. Flame retardant chemical composition was prepared from phosphorus-nitrogen additives (P-N). P-N additives composition was a colourless viscous liquid miscible with water. P-N concentrations were decreased with the increasing water content. Retention and density of RPUF-P-N samples were increased with the increased concentration of P-N for optimum impregnation time of 20 min. Retention and density of RPUF samples with optimum impregnation time were increased up to 62.98% and 80.17 kg/m<sup>3</sup> respectively. The results of morphology show that the cell size of impregnated RPUF samples was decreased from 357 to 285 mm. The cell size was decreased by the increased thickness of cell wall which may be due to the deposition of P-N on the cell walls and surfaces. Elemental analysis of RPUF-P-N shows the introduction of phosphorus and nitrogen into the RPUF backbone. Thermal behaviour shows that RPUF and RPUF-P-N samples were degraded through two and three stages process under nitrogen and air atmosphere respectively. Third stage is attributed to combustion under air. Thus, degradation process is more complex in air than nitrogen. RPUF-P-N samples are decomposed comparatively at lower temperature than RPUF which is resulted into large amount of high temperature stable char residue. This char residue acts as insulating blanket and renders RPUF-P-N fire retardant. The results of extent burnt, burning rate and PML under flammability test indicate that an optimum 90% P-N concentration is adequate to render RPUF fire retardant. RPUF samples containing 46.59% P-N retention exhibit 46.6% increase in the density, however, remarkable decrease in extent burnt (66.25%), burning rate (90.19%) and PML (91.18%) were observed under flammability test. Thus, it can be concluded that P-N impregnation introduces the phosphorus-nitrogen additives into the RPUF structure which is confirmed by the enhanced thermal stability and fire retardancy. Overall, it is concluded that P-N additives impregnated fire retardant rigid polyurethane foam can be used for buildings insulation with added advantage of total safety from fire.

## ACKNOWLEDGEMENT

The author is grateful to the Director, Central Building Research Institute for his encouragement and kind support.

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