

# Effect of Phosphorus-Nitrogen Additives on Fire Retardancy of Rigid Polyurethane Foams

Harpal Singh,<sup>1</sup> A. K. Jain,<sup>2</sup> T. P. Sharma<sup>1</sup>

<sup>1</sup>Fire Research Laboratory, Central Building Research Institute, Roorkee 247667, India

<sup>2</sup>Department of Chemistry, Indian Institute of Technology, Roorkee 247667, India

Received 6 June 2007; accepted 14 February 2008

DOI 10.1002/app.28324

Published online 12 May 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A flame retardant composition was prepared from phosphorus-melamine-urea-formaldehyde (PMUF) reaction. The flame retardancy of rigid polyurethane foam (RPUF) was studied by impregnating it with various concentrations of PMUF. Optimum impregnation time, retention and density of RPUF samples with PMUF were also studied. The morphology, elemental analysis, and thermal stability of RPUF and RPUF-PMUF 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 PMUF on the cell walls and surfaces was exhibited by decreased cell size from 357 to 285 ( $\pm 5$ )  $\mu\text{m}$ . CHNS and EDX studies show the introduction of phosphorus and nitrogen into the RPUF-PMUF samples. The degradation of RPUF and RPUF-PMUF samples was occurred through two and three stages in nitrogen and air, respectively. RPUF-PMUF samples are decomposed com-

paratively 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-PMUF from fire. Fire performance and smoke density of RPUF and RPUF-PMUF samples were investigated with BS: 4735, ASTM D2863 and ASTM E662, respectively. RPUF-PMUF samples demonstrate reduced extent burnt from 125 to 27 mm, burning rate 2.23–0.44 mm/s and percent mass loss (PML) from 100 to 8.82%. Oxygen index was also increased from 17.8 to 23.8. Dm results obtained during smoke density tests show that RPUF-PMUF generates less and delayed smoke than RPUF under flaming and nonflaming mode. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2718–2728, 2008

**Key words:** rigid polyurethane foams; impregnation; SEM; thermal stability; fire retardant; burning rate; percent mass loss; oxygen index; smoke density; combustion; smouldering

## INTRODUCTION

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 diisocya-

nate converts into yellow smoke containing HCN, and rest of the other groups convert to white smoke containing CO<sub>2</sub> and CO. HCN and CO are the prominent toxicant gases which on inhalation lead to death.<sup>3–6</sup>

Various flame retardants such as phosphorus-halogen mixture, ammonium polyphosphate (APP), and organophosphorus compounds either alone or in combination with nitrogen or silicone have been used to impart flame retardancy to RPUFs.<sup>7–9</sup> These compounds may be incorporated into the foam formulation as reactive or nonreactive additives in the form of phosphorus, nitrogen, and halogen elements. Modesti et al. recently reported the successful incorporation of various combinations of halogen free flame 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 flame retardants containing RPUFs give off less-toxic combustion products, thus they are preferred over halogen containing flame 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

Correspondence to: H. Singh (harpal26@yahoo.com).

TABLE I  
Physical Characteristics of the Chemicals Used in the Study

| Chemical           | Phosphoric acid  | Formaldehyde  | Melamine           | Urea  | Water  |
|--------------------|--|---|--------------------|---|--|
| Molecular formula  | $\begin{array}{c} \text{OH} \\   \\ \text{HO}-\text{P}=\text{O} \\   \\ \text{OH} \end{array}$ | $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{H} \end{array}$ |                    | $\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\   \quad    \quad   \\ \text{H}-\text{N}-\text{C}-\text{N}-\text{H} \end{array}$ | $\begin{array}{c} \text{H} \\   \\ \text{H}-\text{O}-\text{H} \end{array}$ |
| Molecular weight   | 98   | 30  | 126.12             | 60.06   | 18   |
| Melting point (°C) | –  | –   | 354                | 132.7   | –  |
| Miscibility        | Miscible with water  | Miscible with water   | Sparingly miscible | Miscible with water   | –  |
| Phosphorus (%)     | ~ 15   | –   | –                  | –   | –  |
| Nitrogen (%)       | –  | –   | ~ 67               | ~ 47  | –  |

any of these problems. The flame 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 catalyze the char formation in the condensed phase. This phosphorus rich char (carbonaceous layer) prevents heat transfer by acting as insulating blanket.<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 crosslinking 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 from phosphoric acid-melamine-urea-formaldehyde (PMUF) reaction and to investigate the effect on the fire retardancy of rigid polyurethane foam impregnated with PMUF. In the PMUF composition, phosphoric acid is the source of phosphorus while melamine and urea are the sources of nitrogen. Earlier such flame retardant compositions have been studied in cellulosic paper and wood,<sup>19</sup> but never in RPUFs to the best of our knowledge. Rigid polyurethane foam RPUF impregnated with PMUF 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 PMUF. The density of RPUF samples impregnated with PMUF was measured as per ASTM D1622. Morphological characteristics, elemental analysis, and thermal behavior properties in nitrogen and air atmosphere of conventional and PMUF 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 and smoke density under flaming and nonflaming mode were evaluated with BS: 4735 and ASTM D2863, and ASTM E662, respectively.

## EXPERIMENTAL

### Materials

Phosphoric acid (88% ortho, GR grade; Merck, Mumbai, India), formalin (37% formaldehyde solution, GR grade; BDH, Mumbai, India), melamine and urea (crystallized, LR grade; Loba, Mumbai, India) and sodium hydroxide (pallets, Merck, Mumbai, India) 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. Some of the physical characteristics of the chemicals used in the study are listed in Table I.

### Preparation of PMUF composition

41% formaldehyde solution (183.0 g, 2.5 mol) mixed with distilled water (126.0 g, 7.0 mol) 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 3N sodium hydroxide solution. The solution was then heated over a water bath until it attains the temperature of 80–85°C. A mixture of urea (60.06 g, 1.0 mol) and melamine (31.53 g, 0.25 mol) was then added incrementally with constant stirring over 20 min. Upon the completion of the addition, the reaction mixture was allowed to reflux for 10 min. The resulting solution was cooled to ambient temperature by putting the flask under cold-water stream. 88% *ortho*-phosphoric acid (111.4 g, 1.0 mol) was then added slowly with constant stirring. During the addition of *ortho*-phosphoric acid, the whole assembly was continuously

**TABLE II**  
**Basic Chemical Formulation of PMUF**

| Chemical                      | Quantity per mole |
|-------------------------------|-------------------|
| <i>Ortho</i> -Phosphoric acid | 1.0               |
| Melamine                      | 0.25              |
| Urea                          | 1.0               |
| Formaldehyde solution         | 3.0               |
| Water                         | 8.0               |

kept under cold-water stream to avoid the heat up of flask due to the heat generated by the reaction of *ortho*-phosphoric acid and mixture solution. The final product was a colorless viscous liquid mixture of phosphorus-melamine-urea-formaldehyde. This viscous mixture was designated as PMUF. The basic formulation used for the PMUF preparation is presented in Table II.

### Sample preparation

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

composition concentrations used for impregnation. RPUF samples impregnated with PMUF are shown in Figure 1(a).

Conventional RPUF and RPUF-PMUF 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-PMUF samples of dimensions 150 × 50 × 13 and 150 × 12.5 × 12.5 mm<sup>3</sup> was investigated by impregnating the three samples with each PMUF concentrations ranging from 0 to 100% with an increment of 10%. After impregnation the RPUF samples were removed from the solution and dried for 24 h at room temperature. Dried RPUF samples were marked across their width by a line (gauge mark) 25 mm from one end. Smoke density of conventional RPUF and RPUF-PMUF samples of size 75 × 75 × 25 mm<sup>3</sup> under flaming and nonflaming mode was investigated by impregnating the samples with maximum PMUF concentration.

### Measurements

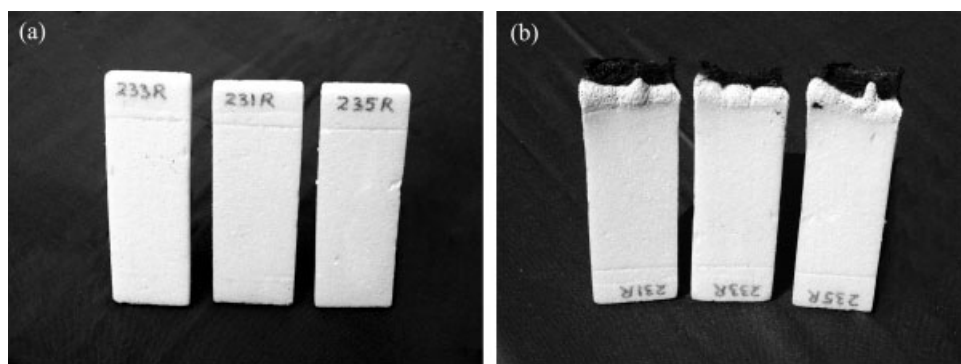
PMUF impregnation extent to the RPUF samples mainly depends upon the concentration, impregnation time, and retention. These three parameters are linked to each other in which impregnation time depends upon the maximum retention, and retention depends on both concentration and impregnation time. Optimum impregnation time was measured on the basis of maximum PMUF retention attained by the RPUF samples with respect to time. Further, optimum impregnation time on the basis of maximum retention of every three RPUF-PMUF samples was calculated and averaged. Retention on each PMUF concentrations were also calculated and averaged.

**TABLE III**  
**Rigid Polyurethane Foam samples (RPUF-PMUF)<sup>a</sup>**  
**Impregnated<sup>b</sup> with Phosphorus-Nitrogen Additives**  
**Based Composition**

| Sample codes<br>(RPUF-PMUF) | PMUF              |           |
|-----------------------------|-------------------|-----------|
|                             | Concentration (%) | Water (%) |
| RPUF-0.0                    | 0.0               | 0.0       |
| RPUF-PMUF                   | 10                | 90        |
| RPUF-PMUF                   | 20                | 80        |
| RPUF-PMUF                   | 30                | 70        |
| RPUF-PMUF                   | 40                | 60        |
| RPUF-PMUF                   | 50                | 50        |
| RPUF-PMUF                   | 60                | 40        |
| RPUF-PMUF                   | 70                | 30        |
| RPUF-PMUF                   | 80                | 20        |
| RPUF-PMUF                   | 90                | 10        |
| RPUF-PMUF                   | 100               | 0.0       |

<sup>a</sup> PMUF denotes phosphorus-melamine-urea-formaldehyde composition.

<sup>b</sup> 20 min optimum impregnation time.



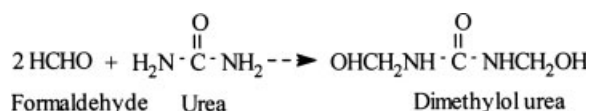
**Figure 1** Photographs of PMUF impregnated RPUF samples (RPUF-PMUF): (a) before flammability test and (b) after flammability test.

The density of conventional RPUF and RPUF-PMUF samples was measured according to ASTM D1622. The size (length $\times$ width $\times$ thickness) of the specimen was  $30 \times 30 \times 30 \text{ mm}^3$ , respectively. Conventional RPUF and RPUF-PMUF specimens were conditioned at  $25^\circ\text{C}$  and 55% relative humidity for 48 h prior to their density measurement. The density of five specimens per sample were measured and averaged.

The morphology of conventional RPUF and RPUF-PMUF samples was observed with Leo (Cambridge, UK) 438 VP 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 PMUF deposition on the cell walls, surfaces and the difference in the shape and size of the cells between conventional RPUF and RPUF-PMUF 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-PMUF samples was carried out with CHNS analyzer (Elementar Andysensysteme GmbH VarioEL III, Germany) and EDX. RPUF and RPUF-PMUF samples powder were mixed with oxidizing agent and dropped into the CHNS chamber at about  $700^\circ\text{C}$ . 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 PMUF impregnation. Thermal properties of conventional RPUF and RPUF-PMUF samples were measured on a TGA/DTG/DTA apparatus (Pyris Diamond, PerkinElmer, Shelton, CT). 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  $1000^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  in nitrogen and air atmosphere at a flow rate of  $200 \text{ mL}/\text{min}$ . After complete heating of the samples TGA, DTG and DTA curves obtained were taken for analysis.

The flammability characteristics of conventional RPUF and RPUF-PMUF samples were evaluated according to BS: 4735 and ASTM D2863. The specimens were weighed before placing horizontally on support gauge inside the noncombustible chamber. The farthest end away from gauge mark of the specimen was exposed for 60 s to 10 mm diameter wing top fitted LPG burner of 38 mm nonluminous flame height. Exposed RPUF-PMUF 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. Oxygen index (OI) of conventional RPUF and RPUF-PMUF samples was carried out with Stanton Redcroft FTA, flammability apparatus, (UK). OI was determined by igniting the specimen in the minimum level of oxygen in an oxygen-nitrogen mixture which supports the candle like burning of the test specimen. The specimens were clamped vertically exactly in the center of the column and 100 mm below the top of the open column. The limiting oxygen concentration is always approached from both sides to establish the OI. The tip of the specimen is ignited in given oxygen concentration atmosphere and maintained for at least 30 s. If the sample burns for 3 min or pass the mark, the oxygen concentration is gradually reduced. Conversely, if the specimen is extinguished in less than 3 min or covers a smaller burning area, the oxygen concentration is increased. During this procedure an oxygen concentration is reached at which sample extinguished at specified length and time and this is taken as the OI. After complete flammability exposure OI of five specimens per sample was measured and averaged. Smoke density of conventional RPUF and RPUF-PMUF samples was measured under flaming and nonflaming mode according to ASTM E662. Specific optical density (smoke concentration) measurement is made of the attenuation of a light beam (transmittance) by smoke accumulating within a closed chamber due to non-





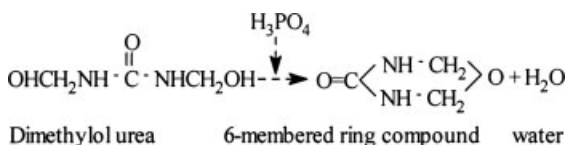
**Scheme 1** Methylation reaction of formaldehyde and urea.

flaming decomposition and flaming combustion of conventional RPUF and RPUF-PMUF samples. The specimens were mounted vertically inside the non-combustible chamber. The specimens were exposed to electrically heated radiant heat source in the presence of six tube LPG burner and, electrically heated radiant heat source for 20 min under flaming and nonflaming mode respectively. After complete exposure percent transmittance (pT) and specific optical density ( $D_s$ ) of three specimens per sample under each mode were measured and averaged.

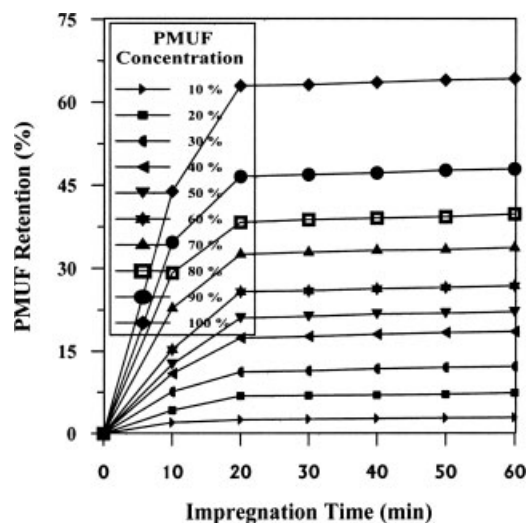
## RESULTS AND DISCUSSION

### PMUF composition

Chemical reactions involved in the preparation of PMUF composition were already studied. It was found that 1 mol of urea in alkaline medium reacts with 1 mol of formaldehyde to form monomethylol urea. Similarly to urea, melamine in alkaline medium reacts with formaldehyde to yield monomethylolated product. When the amount of formaldehyde is increased to 2 mol, 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 80–85°C, the end product was dimethylol and no monomethylol product was formed. Thus the major intermediates in the PUMF composition are  $N,N'$ -dimethylolated urea and  $N,N'$ -dimethylolated melamine. IR spectrum of dimethylolated products exhibited that substitution occurred on the carbon double bond. NMR spectrum of dimethylolated products suggests that when phosphoric acid was added, the hydroxyl proton was no longer coupling with the methylene protons, and most probably 1 mol of water was eliminated to give a 6-membered ring compound (Schemes 1 and 2). Polymerization of this ring compound occurred subsequently which probably acts as fire retardant.<sup>19,21</sup>



**Scheme 2** Dehydration reaction of dimethylol urea.



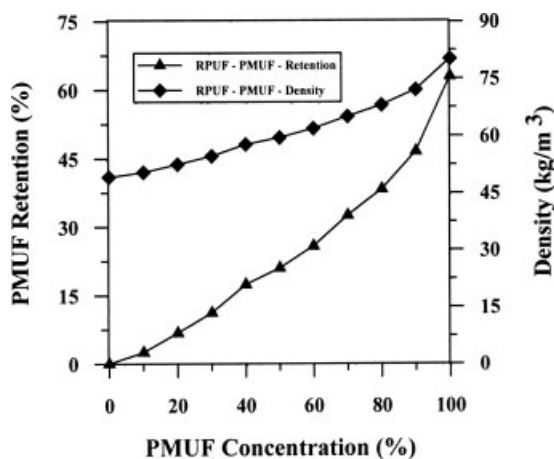
**Figure 2** Effect of PMUF concentration and impregnation time on retention of RPUF samples (RPUF-PMUF).

### Concentration, impregnation, retention, and density

The add-on of phosphorus-melamine-urea-formaldehyde (PMUF) composition to the RPUF samples was mainly measured from PMUF concentration, impregnation time, and retention. Results presented in Figure 2 showed that the retention of RPUF samples was ranged from 1.98 to 64.29% when they were impregnated with 10–100% PMUF concentration for 10–60 min, respectively. After 20 min impregnation the retention of RPUF samples were ranged from 1.98–62.98% with 10–100% PMUF 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 PMUF solution 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-PMUF 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 PMUF solution increases their densities up to 62.98%.

### Morphology

The cross-sectional surfaces of RPUF and RPUF-PMUF samples were observed at the similar magnifi-



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

cation under SEM. Micrographs of the RPUF and RPUF-PMUF samples are shown in Figure 4(a,b). As shown in Figure 4(a), RPUF sample has the polyhedral and spherical cell structure of  $357 (\pm 5) \mu\text{m}$  average cell size. Figure 4(b) shows the deposition of PMUF on the cell surfaces in addition to the polyhedral and spherical cell structure of RPUF. The average cell size of RPUF-PMUF sample was reduced to  $285 (\pm 5) \mu\text{m}$ . This suggests that the decrease in the cell size may be due to the deposition of PMUF on the cell walls also. The PMUF deposition on the RPUF skeleton is further confirmed by the fact that polyurethane phase is optically transparent.<sup>22</sup> Thus PMUF was deposited on the cell surfaces and walls of impregnated RPUF sample.

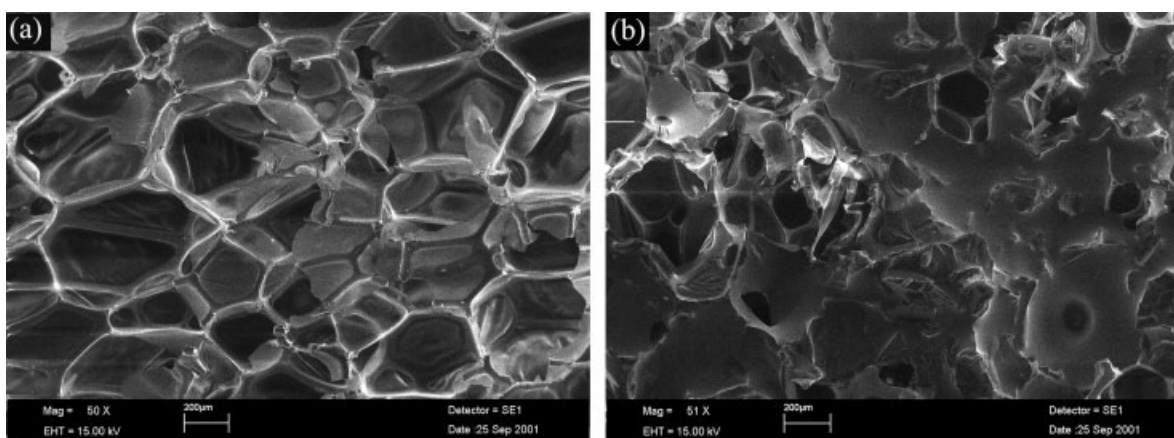
#### Elemental analysis

The elemental analysis results of the RPUF and RPUF-PMUF samples obtained with CHNS analyser and EDX are compiled in Table IV which shows the

presence of various elements. The elements which are present in the minor quantities are not shown 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-PMUF 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 PMUF composition.

#### Thermal analysis

TGA/DTG/DTA profiles for conventional RPUF and RPUF-PMUF samples in nitrogen and air atmosphere are shown in Figures 5(a,b) and 6(a,b), respectively. The data of the TGA/DTG/DTA investigations are summarized in Table V. DTG curves of RPUF and RPUF-PMUF 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-PMUF samples degrade through same process and degradation mechanism in air is much more complex than that in nitrogen.<sup>4,23</sup> In nitrogen atmosphere, RPUF sample does not show distinct weight loss until the temperature rises to  $225^\circ\text{C}$ , whereas, the degradation of RPUF-PMUF begins at  $180^\circ\text{C}$ . During first stage, the rate of weight loss of RPUF begins to increase gradually to a maximum between 285 and  $310^\circ\text{C}$  through two successive decomposition processes. RPUF-PMUF begins to de-



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

TABLE IV  
Elemental Analysis of Conventional and PMUF Impregnated RPUF Samples

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

<sup>a</sup> ( $\pm 0.05\%$ ).

<sup>b</sup> Conventional RPUF.

<sup>c</sup> Phosphorus-melamine-urea-formaldehyde impregnated RPUF.

grade between 180 and 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-PMUF starts between 400 and 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-PMUF 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 contain carbon, and condensed aromatic contents, because biuret, allophanate, urea, urethane, and disubstituted urea are the thermally weakest links in the polyurethane network.<sup>4,5</sup> On the basis of the TGA/DTG/DTA traces, it can be seen that decomposition of RPUF-PMUF begins at lower temperature than conventional RPUF. This suggests that RPUF and PMUF react first. The lower initial thermal decomposition temperature and correspondingly higher amount of stable char yield may indicate that PMUF 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 tempera-

ture 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, 350–478, and 480–650°C which are consistent with the previous studies conducted and reported in the literature.<sup>3–4,9,25</sup> RPUF-PMUF 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 and 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>4,6,23</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-PMUF 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-PMUF sample degrades exothermically at 521°C. Third steps are from the combustion which leads to 18% high temperature char residues at

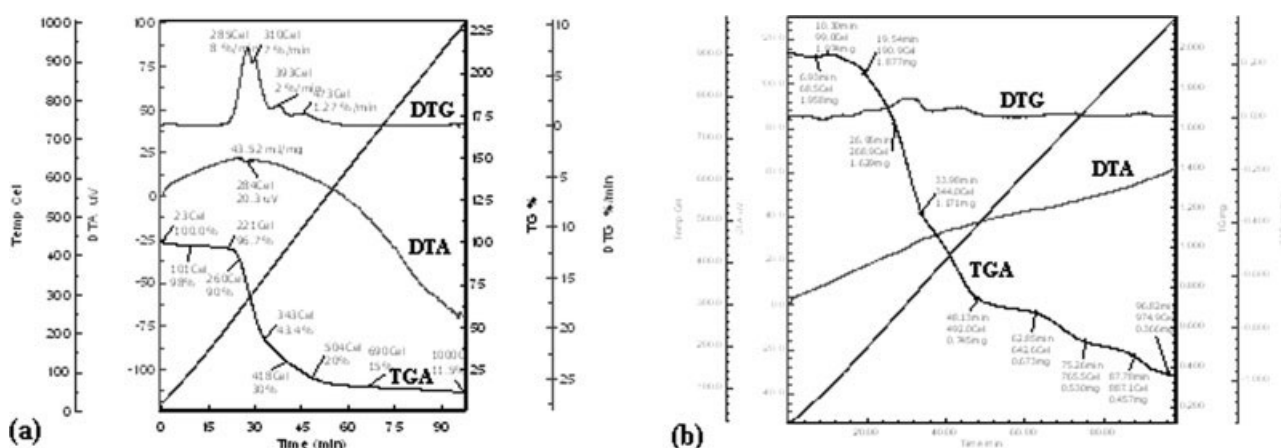


Figure 5 Thermograms of RPUF samples in nitrogen atmosphere: (a) conventional RPUF and (b) RPUF-PMUF impregnated.



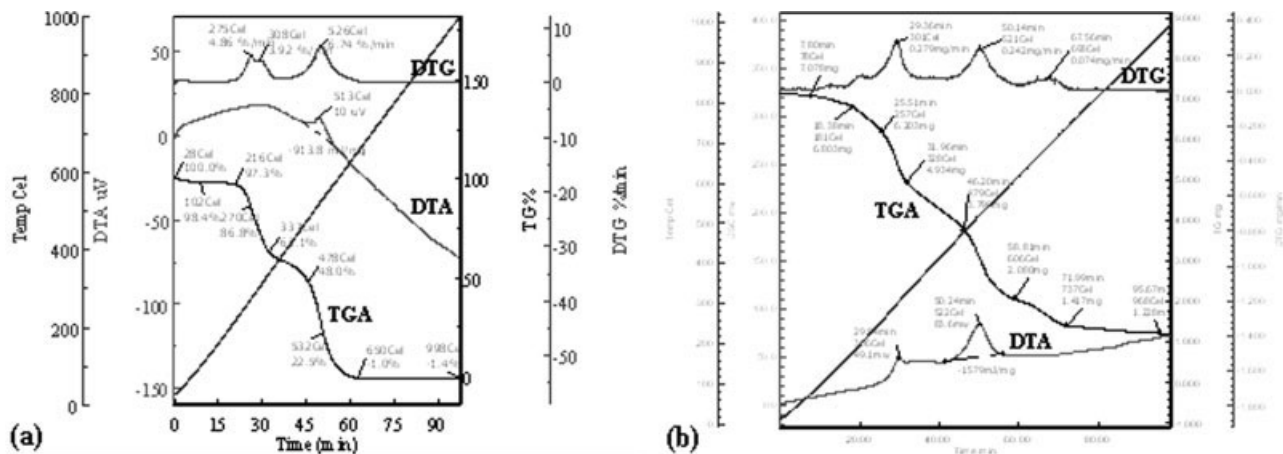


Figure 6 Thermograms of RPUF samples in air atmosphere: (a) conventional RPUF and (b) RPUF-PMUF impregnated.

900°C. The increased char residue quantity may be due to the phosphorus-nitrogen additives. The presence of phosphorus-nitrogen additives into the RPUF-PMUF 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-PMUF 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-PMUF 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>

### Fire behavior

Fire performance of RPUF and RPUF-PMUF samples and their comparison is mainly measured from extent burnt, burning rate, 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-PMUF samples with respect to PMUF concentrations are shown in Figures 7 and 8, respectively. Figure 7 presents the results as expected with an increasing concentration of PMUF from 0 to 100%, the extent burnt and burning rate were decreased from 125 to 27 mm and 2.23–0.44 mm/s, respectively. However, exponential difference was observed between RPUF and RPUF samples impregnated with minimum (10%) PMUF 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

TABLE V  
Thermal Behavior and Thermal Stability of Conventional and PMUF Impregnated RPUF Samples in Nitrogen and Air Atmosphere

| Sample codes           | A/N            | $T_{on}$ (°C) | $T_{1max}$ (°C) | $R_{1max}$ (%/min) | $T_{2max}$ (°C) | $R_{2max}$ (%/min) | $T_{3max}$ (°C) | $R_{3max}$ (%/min) | $Y_c$ (%) |
|------------------------|----------------|---------------|-----------------|--------------------|-----------------|--------------------|-----------------|--------------------|-----------|
| 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-PMUF <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        |

A/N denotes the air and nitrogen atmosphere.

$T_{on}$  denotes on-set degradation temperature.

$T_{1max}$ ,  $T_{2max}$  and  $T_{3max}$  denotes maximum degradation temperatures in first, second and third stage respectively.

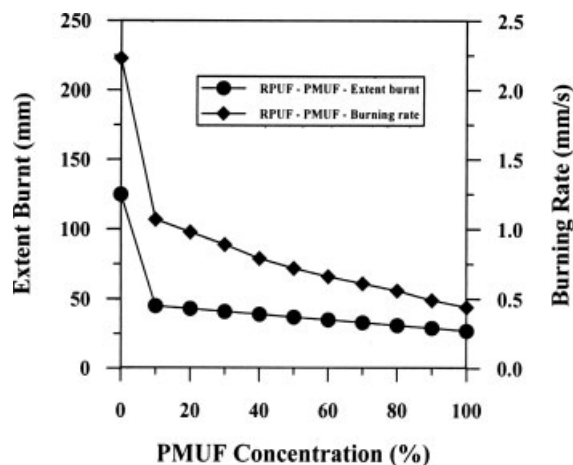
$R_{1max}$ ,  $R_{2max}$  and  $R_{3max}$  denotes maximum rate of degradation in stage first, second and third stage respectively.

$Y_c$  denotes the char yield at 900°C.

<sup>a</sup> Conventional RPUF.

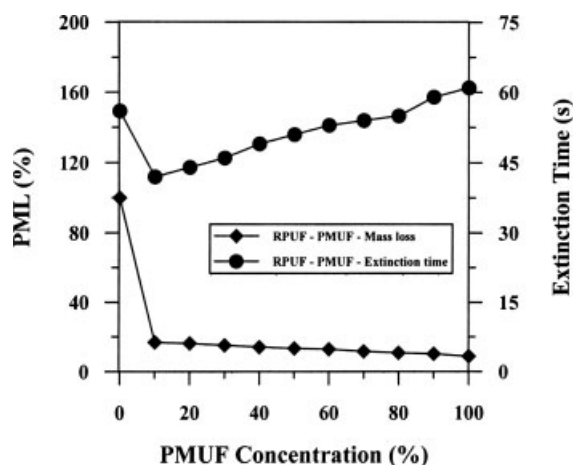
<sup>b</sup> Phosphorus-melamine-urea-formaldehyde (PMUF) impregnated RPUF.





**Figure 7** Effect of PMUF concentration on extent burnt and burning rate of conventional and PMUF impregnated RPUF samples.

extent burnt and burning rate are almost linear with the increase of PMUF concentration. However, when PMUF concentration increases over 90% up to 100%, there is an increase of 16.39% in the retention of RPUF-PMUF, 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 PMUF concentration. As shown in Figure 8, the increasing concentration of PMUF from 0 to 100% reduces the PML from 100 to 8.82%, but extinction time increases slightly from 56 to 60 s, respectively. RPUF and RPUF samples impregnated with minimum (10%) PMUF concentration show great differences in their PML and extinction time which are 100%, 56 s and 16.92%, 40 s, respectively. The rate of PML reduction is almost linear to 90% PMUF concentration and above this PML reduces

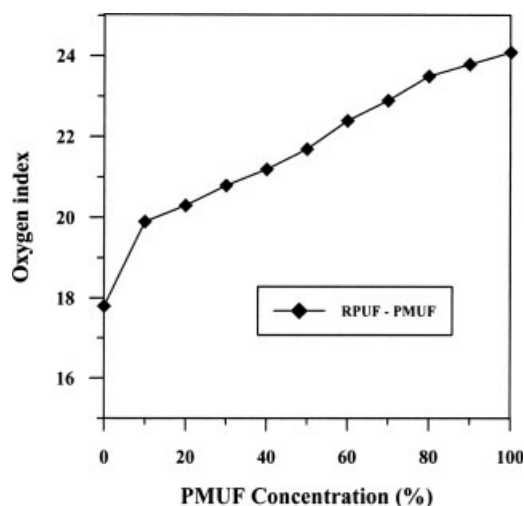


**Figure 8** Effect of PMUF concentration on PML and extinction time of conventional and PMUF impregnated RPUF samples.

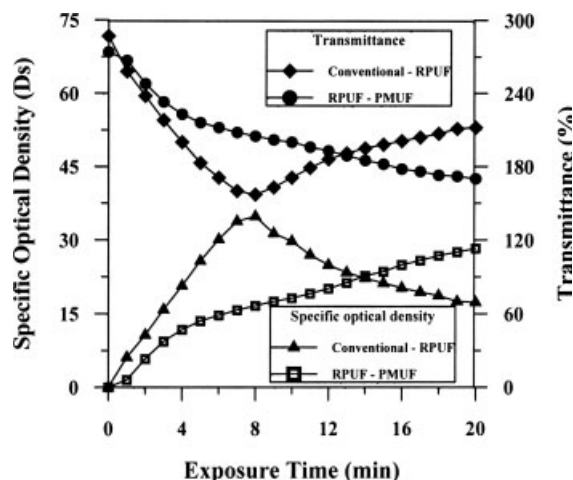
slightly as the concentration increases to 100%. RPUF samples in flammability test are consumed up to gauge mark (125 mm) in 56 s. For comparison, 56 s is considered as extinction time of RPUF. The extinction time of RPUF sample reduces to 42 s with minimum PMUF concentration, however, increases to 61 s with maximum concentration. This slightly different flame extinction behavior of RPUF-PMUF 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 PMUF 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 lead 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-PMUF samples, PMUF concentration of 90% can be considered as optimum.

### Oxygen index

Oxygen index (OI) is a fundamental tool in basic research on polymer combustion and mechanism of fire retardancy. OI also provides an evaluation of intrinsic flammability of the polymeric materials.<sup>26</sup> Thus, flammability of RPUF and RPUF-PMUF samples is also evaluated by determining their oxygen indexes with respect to various PMUF concentrations and values are presented in Figure 9. OI of



**Figure 9** Effect of PMUF concentration on oxygen index (OI) of conventional and PMUF impregnated RPUF samples.



**Figure 10** Smoke density of conventional and PMUF impregnated RPUF samples under flaming mode.

RPUF is 17.8 which increase from 19.9 to 24.1 as the PMUF concentrations are increased from 10 to 100%, respectively. An OI of RPUF-PMUF is probably increased due to the presence of phosphorus and nitrogen into the PMUF composition. Phosphorus and nitrogen have synergistic effect between them which enhances the OI of RPUF-PMUF (Wang, 2005). The trend of these data shows that OI increases with increasing concentrations of PMUF.

### Smoke density

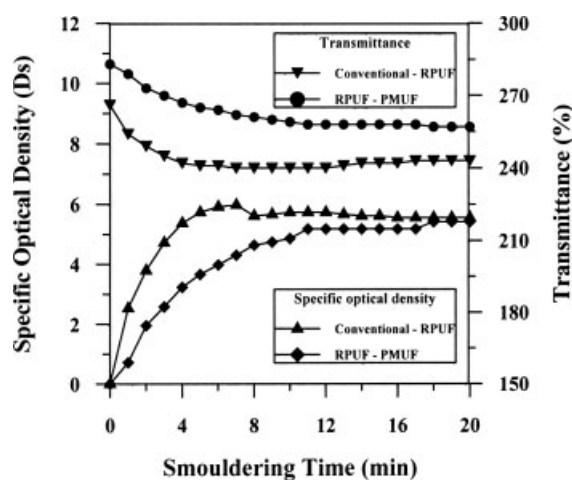
Figures 10 and 11 demonstrate the smoke evolution from the RPUF and RPUF-PMUF under flaming and nonflaming mode, respectively. Smoke density and evolution pattern are expressed in terms of specific optical density ( $D_s$ ) and percent transmittance (pT) from RPUF and RPUF-PMUF under flaming and nonflaming mode. As shown in Figure 10, the pT of RPUF decreases from 287 to 157 and  $D_s$  increases from 0 to 34.82 after 8 min of exposure. After 8 min, pT again increases to 212 and  $D_s$  decreases to 17.34 at the end of exposure. These results indicate that RPUF generates maximum smoke after 8 min exposure and the quantity of smoke decreases slightly towards the end of exposure. Under similar exposure conditions, the pT of RPUF-PMUF decreases from 274 to 170 and  $D_s$  increases from 0 to 28.28 after complete 20 min combustion. The pT and  $D_s$  values exhibit that RPUF-PMUF generates maximum smoke towards the end of exposure. The above results show that maximum specific optical density ( $D_m$ ) of RPUF and RPUF-PMUF are 34.82 and 28.28, respectively, as maximum value of  $D_s$  is referred as  $D_m$ . The values of  $D_m$  indicate that RPUF-PMUF generates less smoke than that of RPUF. As shown in the Figure 11, during RPUF smouldering under nonflaming mode the pT decreases and  $D_s$  increases to

5.98 after 7 min which remains stable up to 12 min. A little increase in pT and decrease in  $D_s$  from 5.98 to 5.56 are observed towards the end. The trend of these data shows that RPUF generates maximum smoke between 7 and 12 min which reduces slightly in the end. The RPUF-PMUF exhibits that pT decreases and  $D_s$  increases up to 11 min and remain stable up to 17 min. A very little decrease in pT and increase in  $D_s$  are observed at the end of smouldering. Thus RPUF-PMUF generates maximum smoke between 11 and 17 min which further increases slightly toward the end. The  $D_m$  values of RPUF and RPUF-PMUF shown are 5.98 and 5.42, respectively. These results indicate that RPUF generates rapid and more smoke in the beginning whereas, RPUF-PMUF generates slow and less smoke toward the end of smouldering.

It is quite clear that RPUF and RPUF-PMUF generate more smoke under flaming than nonflaming mode. However, RPUF-PMUF generates less and delayed smoke than RPUF under both flaming and nonflaming mode. The generation of less and delayed smoke from RPUF-PMUF may be due to the synergistic effect between phosphorus and nitrogen.<sup>7</sup> The suppression of smoke in RPUF by the synergistic effect between phosphorus-nitrogen is further confirmed by the earlier research work which describes that the presence of phosphorus alone in burning foam increases the production of smoke.<sup>27</sup>

### CONCLUSIONS

To understand the effect of PMUF composition on the structure, thermal stability, flammability characteristics and smoke density of RPUF, large number of RPUF samples impregnated with various concentrations of PMUF were investigated using SEM, CHNS analyzer and energy dispersive X-rays (EDX),



**Figure 11** Smoke density of conventional and PMUF impregnated RPUF samples under nonflaming mode.

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 *ortho*-phosphoric acid, melamine, urea and formaldehyde solution (PMUF). PMUF was a colorless viscous liquid miscible with water. PMUF concentrations were decreased with the increasing water content. Retention and density of RPUF-PMUF samples were increased with the increased concentration of PMUF 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 showed that the cell size of impregnated RPUF samples was decreased from 357 to 285 μm. The cell size was decreased by the increased thickness of cell wall which may be due to the deposition of PMUF on the cell walls and surfaces. Elemental analysis of RPUF-PMUF shows the introduction of phosphorus and nitrogen into the RPUF backbone. Thermal behavior shows that RPUF and RPUF-PMUF samples were degraded through two and three stage 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-PMUF 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-PMUF fire retardant. The results of extent burnt, burning rate, PML and oxygen index under flammability tests indicate that an optimum 90% PMUF concentration is adequate to render RPUF fire retardant. RPUF samples containing 46.59% PMUF 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. Oxygen index was also increased from 17.8 to 23.8. Dm results obtained during smoke density tests show that RPUF-PMUF generates less and delayed smoke than conventional RPUF under flaming and nonflaming mode. However, the generation of smoke is more under flaming than nonflaming mode. Thus, it can be concluded that PMUF impregnation introduces the phosphorus-nitrogen additives into the RPUF structure which is confirmed by the enhanced thermal stability, fire retard-

ancy and reduced level of smoke generation under flaming and nonflaming mode.

The authors are grateful to the Director, Central Building Research Institute for his encouragement and kind support. They also acknowledge the services rendered by Shri Rakesh Kumar.

## References

- Oertel, G. *Polyurethane Handbook*; Hanser Publisher: New York, 1985.
- Szycher, M. *Handbook of Polyurethanes*; CRC Press: Washington, DC, 1999.
- Lefebvre, J.; Bastin, B.; Bras, M. L.; Duquesne, S.; Paleja, R.; Delobel, R. *Polym Degrad Stab* 2005, 88, 28.
- Tang, Z.; Valer, M.; Anderson, J. M.; Miller, J. W.; Listemann, M. L.; McDaniel, P. L.; Morita, D. K.; Furlan, W. R. *Polymer* 2002, 43, 6471.
- Levchik, S. V.; Weil, E. D. *Polym Int* 2004, 53, 1585.
- Pielichowski, K.; Kulesza, K.; Pearce, E. M. *J Appl Polym Sci* 2003, 88, 2319.
- Leu, T. S.; Wang, C. S. *J Appl Polym Sci* 2004, 92, 410.
- Yang, C. P.; Hsiao, S. H. *J Appl Polym Sci* 1988, 36, 1221.
- Duquesne, S.; Bras, M. L.; Bourbigot, S.; Delobel, R.; Camino, G.; Eling, B.; Lindsay, C.; Roels, T.; Vezin, H. *J Appl Polym Sci* 2001, 82, 3262.
- Modesti, M.; Lorenzetti, A.; Simioni, F.; Checchin, M. *Polym Degrad Stab* 2001, 74, 475.
- Modesti, M.; Lorenzetti, A. *Polym Degrad Stab* 2002, 78, 167.
- Modesti, M.; Lorenzetti, A. *Polym Degrad Stab* 2002, 78, 341.
- Modesti, M.; Lorenzetti, A. *Eur Polym J* 2003, 39, 263.
- Horrocks, A. R.; Zhang, J.; Hall, M. E. *Polym Int* 1994, 33, 303.
- Wang, C. S.; Lin, C. H. *Polymer* 1999, 40, 747.
- Liu, Y. L.; Hsine, G. H.; Chiu, Y. S.; Jeng, R. J.; Ma, C. *J Appl Polym Sci* 1996, 59, 1619.
- Camino, G.; Costa, L.; Luda di Cortemiglia, M. P. *Polym Degrad Stab* 1991, 33, 131.
- Grassie, N.; Zulfiqar, M. In *Developments in Polymer Stabilization*; Scott, G., Ed.; Kluwer Academic Publishers: Dordrecht, 1979; pp 197–217.
- Juneja, S. C. *Forest Prod J* 1972, 22, 17.
- Singh, H.; Sharma, T. P.; Jain, A. K. *J Appl Polym Sci* 2007, 106, 1014.
- Fang, D. P. C.; Juneja, S. C.; Doyle, E. E. In *International Symposium on Flammability and Fire Retardants*, Cornwall, Ontario, Canada; Bhatnagar, V. M., Ed.; Cornwall, Ontario Canada; Technomic Publishing Company Co. Inc.: Westport, CT, 1974; p 238.
- Kageoka, M.; Tairaka, Y.; Kodama, K. *J Cell Plast* 1997, 33, 219.
- Li, X.-B.; Cao, H.-B.; Zhang, Y. *J Appl Polym Sci* 2006, 102, 4149.
- Wang, T.; Cho, Y. L.; Kuo, P. L. *J Appl Polym Sci* 2001, 82, 343.
- Matuschek, G. *Thermochim Acta* 1995, 263, 59.
- Camino, G.; Costa, L.; Casorati, E.; Bertelli, G.; Locatelli, R. *J Appl Polym Sci* 2003, 35, 1863.
- Finhorn, I. *Polymer Conference*, Wayne State University, 1965.