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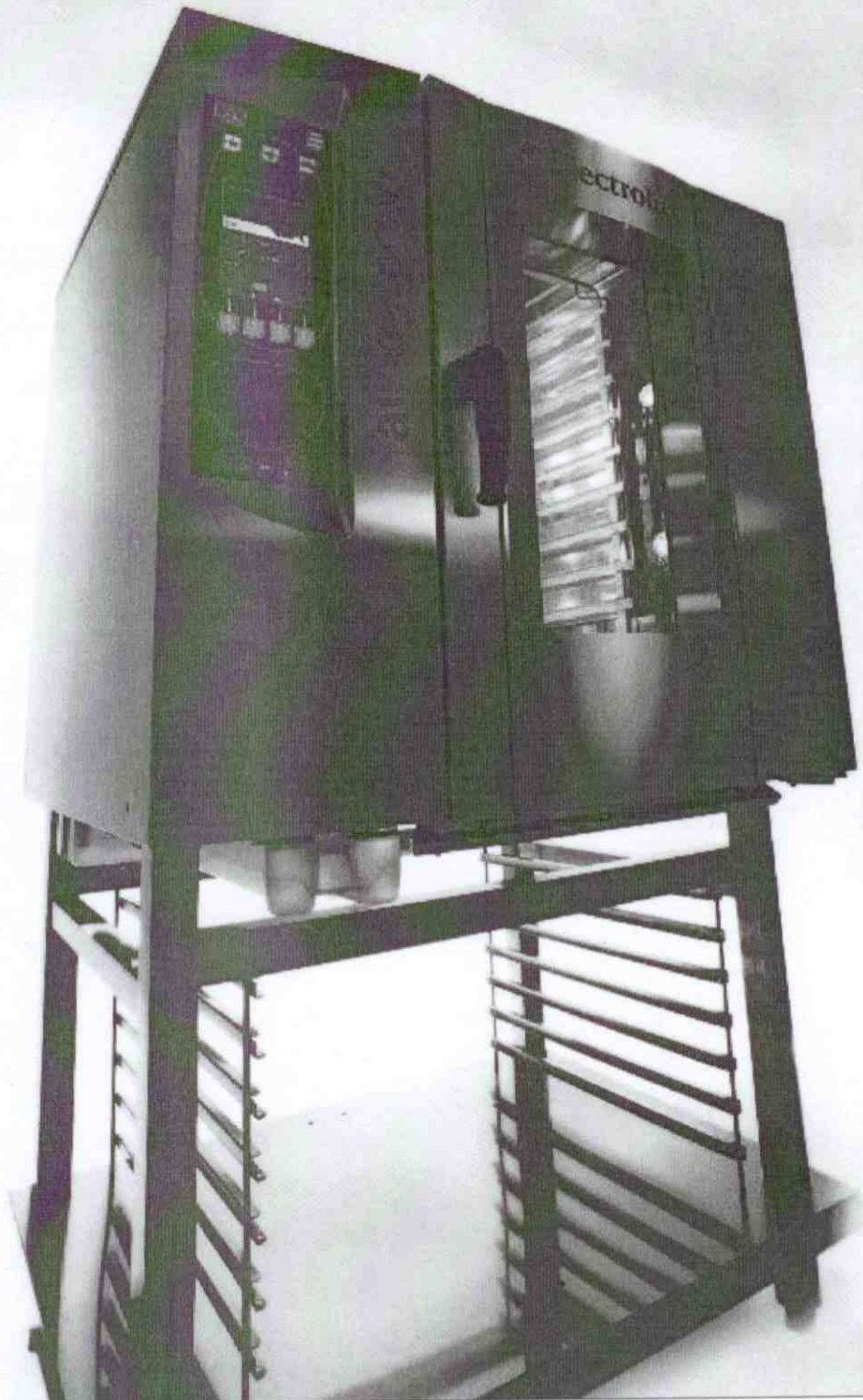
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by Harpal Singh, *Fire Research Laboratory, Central Building Research Institute*, and A. K. Jain, *Department of Chemistry, Indian Institute of Technology*

Effects of Blowing Agents on the Characteristics of Rigid Polyurethane Foam

Research shows the quantity of physical and chemical blowing agents directly affects the density, cell morphology, and flammability of RPUF samples.

► Rigid polyurethane foam (RPUF) samples were prepared from crude 4, 4'-diphenylmethane diisocyanate (CMDI), polyether polyol, triethylene diamine (TED), 1, 4-butane diol, polysiloxane ether, methylene chloride, and water. The density of RPUF samples was measured according to ASTM D1622. The density of RPUF samples blown by chemical blowing agent, physical blowing agent, and mixture of chemical and physical blowing agents ranged from 240.1 to 33.4 kg/m³ with an increase of blowing agent contents. The cell morphology of the RPUF samples was investigated with scanning electron microscopy (SEM). SEM results exhibit the average increase in the cell size of the RPUF samples from 162 to 278 μm with the increased blowing agent contents. The flammability performance of RPUF samples was investigated with BS: 4735. The flammability results indicate that extent burnt and percent mass loss (PML) were unchanged; however, burning rate decreases and burning time increases as the density increased. The increasing quantity of chemical blowing agent increases the burning rate and decreases the burning time but does not have any effect on the extent burnt and PML of RPUF samples. It is concluded that the quantity of chemical blowing agent directly affects the density, cell morphology, and flammability of RPUF samples.

Introduction

Structurally, polyurethane is an extremely large and complex polymer that may contain aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea, biuret, allophanate, carbodiimide, and isocyanurate groups in addition to the urethane linkages. Depending upon the ingredients and composition, polyurethane can be used for manufacture of an extremely wide range of products such as adhesives, coatings, elastomers, and flexible and rigid foams. The cell geometry of rigid polyurethane foams is closed cell. The closed cell foams are generally rigid in nature and are most suitable for thermal insulation due to their low thermal conductivity, low density, high strength-to-weight ratio, and low moisture permeability. Some typical engineering applications of RPUF are in transportation, refrigeration technology and appliances, building construction industry, automotive industry, packaging, carpet underlay, and sporting goods.

RPUF is prepared by mixing polyol with catalyst, surfactant, chain extender, and chemical and physical blowing agents in the first stage. In the second stage, blended polyol is mixed with diisocyanate to react. During

Chemicals	Functionality	Equivalent Weight (gr/mol)	Comments
Crude 4, 4'-Diphenylmethane diisocyanate (CMDI)	2.2	134.0	NCO content = 31.32 %
Polyether Polyol	4.3	127.5	OH value = 440 mg KOH/g
Triethylene diamine (TED)	—	—	Blowing catalyst
Stannous octoate (Tin)	—	—	Gelling catalyst
Water	2.0	9.0	Chemical blowing agent
Polysiloxane ether	—	—	Silicone surfactant
1, 4-butane diol (BD)	2.0	45.1	Chain extender
Methylene chloride	—	—	Physical blowing agent

Table 1. Physical characteristics (provided by the suppliers and manufacturers) of the chemicals used in the present study.

mixing, some air bubbles are introduced into the mixture and they serve as nuclei for foam cells. The bubbles are stabilized by silicone surfactant. The foaming of the RPUF can be carried out either by chemical blowing agent or physical blowing agent, or by the mixture of both. Water is one of the most widely used of all chemical blowing agents. It reacts with diisocyanate and produces unstable carbamic acid initially, which immediately decomposes to an amine and carbon dioxide. This carbon dioxide diffuses into the already present air bubbles, which results in the rise of foam due to the increase in bubble size. At the same time, the viscosity of the medium increases due to polymerization and gelation.

The widely used physical blowing agents are chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). RPUF formation is principally based on the reaction of polyol with diisocyanate. The reaction is exothermic, and the heat of reaction is used to form a cellular structure by evaporation of the physical blowing agent. Isocyanate-urethane and isocyanate-urea reactions lead to branching and cross-linking in the RPUF structure by forming allophanate and biuret, respectively.

The present study deals with the chemical composition and preparation of RPUF. The effects of chemical blowing agent, physical blowing agent, and mixture of chemical and physical blowing agents on density, cell morphology, and flammability of RPUF samples were investigated. RPUF was prepared from crude 4, 4'-diphenylmethane diisocyanate (CMDI) with a functionality of 2.2 and polyether polyol with a functionality of 4.3 and hydroxyl value 440. CMDI and polyether polyol have a major impact on the properties of the RPUF. Triethylene diamine (TED), stannous octoate, 1, 4-butane diol, and polysiloxane ether were used as amine catalyst, tin catalyst, chain extender, and surfactant, respectively, during RPUF preparation. Water as chemical blowing agent and methylene chloride as physical blowing agent were used. The effects of chemical and physical blowing agents were studied by varying the quantities of

Ingredients	Parts per 100 polyether polyol by weight (php)
Polyether polyol	100.00
Triethylene diamine (TED)	0 - 0.9 ^a
Water (chemical blowing agent)	0 - 3.0 ^b
Polysiloxane ether	0 - 2.0 ^c
1, 4-butane diol (BD)	0 - 30 ^d
Methylene chloride (physical blowing agent)	0 - 30 ^e
Crude 4, 4'-diphenylmethane diisocyanate (CMDI)	Stoichiometric +5 %

^a0 - 0.9 parts of triethylene diamine with an increment of 0.1 parts.
^b0 - 3.0 parts water with an increment of 0.5 parts.
^c0 - 2.0 parts polysiloxane ether with an increment of 0.25 parts.
^d0 - 30 parts 1, 4 butane diol with an increment of 2.5 and 5.0 parts.
^e0 - 30 parts methylene chloride with an increment of 5.0 parts.

Table II. Chemical formulation of rigid polyurethane foam (RPUF).

water and methylene chloride during the preparation of RPUF samples. By varying the compositions and amount of chemical blowing agent, physical blowing agent, and mixture of chemical and physical blowing agents, RPUF samples of various densities were obtained.

The main aim of this study was to evaluate the influence of chemical and physical blowing agents on density, cell morphology and flammability characteristics of RPUF samples using scanning electron microscopy (SEM) and BS: 4735 horizontal flammability test.

Materials

The materials and chemicals were obtained from branded and commercial sources. CMDI and polyether polyol were obtained from Industrial Foams Ltd. (Delhi, India). Methylene chloride, 1, 4-butane diol, stannous octoate (stannous 2-ethyl hexanoate), and triethylene diamine [1, 4 diazabicyclo (2, 2, 2) octane] were obtained from E. Merck Ltd. (Mumbai, India), Spectrochem Pvt. Ltd. (Mumbai, India), Sigma Chemicals Co. (St. Louis, MO, U.S.), and Fluka chemie GmbH (Steinheim, Germany), respectively. Prior to the addition into the formulation, amine catalyst was not dissolved in any medium and used as such. Polysiloxane ether was obtained from Sheela Foams Pvt. Ltd. (Ghaziabad, India) and Industrial Foams Ltd. (Delhi, India). Ordinary water was used as chemical blowing agent. The chemicals were used as received. Some of the physical characteristics of the chemicals used are shown in Table I.

RPUF Formulation

Formulation of rigid polyurethane foam (RPUF) is primarily based on polyether polyol, CMDI, triethylene diamine (TED), polysiloxane ether, 1, 4-butane diol, water, and methylene chloride. The amount of polyether polyol was set to 100 parts by weight. The amount of CMDI required for the reaction with polyether polyol, 1, 4-butane diol, and water was calculated from their equivalent weights. About 5% weight excess CMDI was used for the completion of the reaction. This 5% weight excess CMDI is calculated from isocyanate index (NCO/OH = 1.05), which is based on used number of equivalents of diisocyanate, polyether polyol, and water. The amount of amine catalyst, mixture of amine and tin catalysts, and water were varied in order to

obtain desired cream time, gel time, and tack-free time. The amounts of water and methylene chloride were varied and calculated in order to obtain desired foam densities. The amounts of triethylene diamine, polysiloxane ether, 1, 4-butane diol, water, and methylene chloride per 100 parts polyether polyol by weight (php) were selected as optimal after a series of foam preparation experiments was carried out. The amount of 1, 4-butane diol can be varied depending upon the requirement of hard segment and cross-linking into the foam structure. The basic formulation used for the rigid polyurethane foam (RPUF) preparation is presented in Table II.

RPUF Sample Preparation

RPUF samples with different amounts (php) of ingredients were prepared through the one-shot method. Except for the CMDI, all the raw chemicals such as TED, polysiloxane ether, 1, 4-butane diol, water, and methylene chloride were first manually well-blended with polyether polyol for 30 seconds in a stainless steel beaker. CMDI was then added into the blended polyol and mixed for 20 seconds under an overhead electric stirrer. The stirrer speed was set at 3000 rpm throughout the mixing.

After mixing, the reactants were discharged into an open mold (200 × 200 × 250 mm) that was lined with paper to produce free-rise foam. As the reactants mixture was poured into the mold, formation of many very small bubbles was observed, which were dispersed into the reaction mixture. These tiny gas bubbles formed the nuclei into which the blowing gas diffused as the reaction proceeded. The number, size, and distribution of the nuclei determine the final foam structure. The foam cake was then cured for 48 hours at room temperature. Foam can also be cured at elevated temperatures; however, we preferred to perform the curing at room temperature in order to observe the foam properties at ambient processing conditions.

The effect on RPUF densities blown by chemical, physical, and mixtures of chemical and physical blowing agents was investigated by varying the amounts of water and methylene chloride, respectively. The amount of water was varied from 0-3.0 php with an increment of 0.5 php. Similarly, the amount of methylene chloride varied from 0-30 php with an increment of 5 php. The mixture of water and methylene chloride was also used by varying the amount of one blowing agent, whereas the amount of other blowing agent was constant, and vice versa. The amounts of TED, polysiloxane ether, and 1, 4-butane diol were fixed at 0.6, 1.0, and 20 php, respectively, with polyether polyol 100 parts by

Sample codes (RPUF-W-MC)	Polyether polyol	Crude MDI	TED	1, 4-BD	Polysiloxane ether	W	MC
RPUF-0.0-0.0	100	172.8	0.6	20	1.0	0.0	0.0
RPUF-W-0.0	100	180.6	0.6	20	1.0	0.5	0.0
RPUF-W-0.0	100	188.4	0.6	20	1.0	1.0	0.0
RPUF-W-0.0	100	196.2	0.6	20	1.0	1.5	0.0
RPUF-W-0.0	100	204.0	0.6	20	1.0	2.0	0.0
RPUF-W-0.0	100	211.9	0.6	20	1.0	2.5	0.0
RPUF-W-0.0	100	219.7	0.6	20	1.0	3.0	0.0
RPUF-0.0-MC	100	172.8	0.6	20	1.0	0.0	5.0
RPUF-0.0-MC	100	172.8	0.6	20	1.0	0.0	10
RPUF-0.0-MC	100	172.8	0.6	20	1.0	0.0	15
RPUF-0.0-MC	100	172.8	0.6	20	1.0	0.0	20
RPUF-0.0-MC	100	172.8	0.6	20	1.0	0.0	25
RPUF-0.0-MC	100	172.8	0.6	20	1.0	0.0	30

^aParts by 100 parts of polyether polyol.
^bW-MC denotes the amount of chemical blowing agent - physical blowing agent.

Table III. Chemical compositions^a of rigid polyurethane foam (RPUF-W-MC)^b blown with chemical and physical blowing agents contents.

Sample code (RPUF-W-MC)	Polyether polyol	Crude MDI	TED	1,4-BD	Polysiloxane ether	W	MC
RPUF-0.0-0.0	100	172.8	0.6	20	1.0	0.0	0-0.0
RPUF-0.5-MC	100	180.6	0.6	20	1.0	0.5	5-30 ^a
RPUF-1.0-MC	100	188.4	0.6	20	1.0	1.0	5-30
RPUF-1.5-MC	100	196.2	0.6	20	1.0	1.5	5-30
RPUF-2.0-MC	100	204.0	0.6	20	1.0	2.0	5-30
RPUF-2.5-MC	100	211.9	0.6	20	1.0	2.5	5-30
RPUF-3.0-MC	100	219.7	0.6	20	1.0	3.0	5-30

^aParts by 100 parts of polyether polyol.
^b0-30 parts of physical blowing agent with an increment of five parts.

Table IV. Chemical compositions^a of rigid polyurethane foam (RPUF-W-MC) blown with chemical and physical blowing agents mixture.

weight. The amount of CMDI required for the reaction with polyether polyol, 1, 4-butane diol, and water was calculated from their equivalent weights. For the completion of the reaction, 5% excess (NCO/OH = 1.05) CMDI was used. When water is used as blowing agent, it reacts with CMDI to produce disubstituted urea and carbon dioxide. The carbon dioxide inflates the reactants, which results in a cellular structure. Similarly, methylene chloride, when used as blowing agent, boils and evaporates by the heat generated through exothermic reaction of CMDI and polyether polyol and inflates the reactants. Tables III and IV show the chemical compositions of the RPUF samples (RPUF-W-MC) blown by chemical blowing agent, physical blowing agent, and mixture of chemical and physical blowing agents, respectively. In the sample codes, W and MC denote the amounts of chemical blowing agent and physical blowing agent used, respectively.

The effect on cell morphology of RPUF samples was investigated by preparing samples blown with 0.5 and 3.0 php chemical blowing agent and 3 and 30 php physical blowing agent for scanning electron microscopy (SEM). The flammability characteristics of RPUF samples of dimensions 150 × 50 × 13 mm were evaluated by preparing samples with densities ranging from 40.39 to 168.83 kg/m³. RPUF samples blown with 0.5-3.0 php chemical blowing agent in combination with 5-30 php physical blowing agent were also prepared for flammability characteristics investigation. RPUF samples were marked across their width by a line (gauge mark) 25 mm from one end.

Measurements

The density of RPUF samples was measured according to ASTM D1622. The size (length × width × thickness) of the specimen was 30 × 30 × 30 mm, respectively. RPUF 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 was measured and averaged. The morphology of the RPUF samples was observed with LEO (438 VP, UK) scanning electron microscopy (SEM). The samples were cryogenically fractured and gold coated and scanned at 15 kv accelerating voltage to observe the shape and size of the cells. To define the cell size, measured cell sizes were averaged except for the sizes for the largest and smallest cells.

The flammability characteristics of RPUF samples were evaluated according to BS: 4735. 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 seconds to 10-mm-diam wing top fitted LPG burner of 38-mm non-luminous flame height. After the fire exposure is completed, extent burnt, burning rate, percent mass loss (PML), and burning time of three specimens per sample were measured and averaged for analysis.

Density Measurement

The densities of RPUF samples blown with and without chemical and physical blowing agents and mixture of both blowing agents were measured. The density of RPUF samples in the absence of blowing agent was 240.1 kg/m³. The density of RPUF samples (RPUF-W) blown by chemical blowing agent was decreased from 240.1 to 56.5 kg/m³, as the water content increased from 0 to 3.0 php, respectively. The density of the RPUF samples blown by the physical blowing agent decreased from 240.1 to 49.3 kg/m³ as the content of the physical blowing agent increased from 0 to 30 php, respectively. When a mixture of chemical and

physical blowing agents was used, the density of the RPUF samples (RPUF-W-MC) varied from 240.1 to 33.4 kg/m³. Thus, it is quite clear that the density of RPUF samples decreased as the chemical and physical blowing agent contents increased.

Morphology

The cross-sectional surface of the RPUF samples individually blown by 0.5 (RPUF-0.5-0) and 3.0 (RPUF-3.0-0) php chemical blowing agent content and by 5 (RPUF-0-5) and 30 (RPUF-0-30) php physical blowing agent content were observed under SEM. All four RPUF samples were scanned at the similar magnification in the free-rising direction.

RPUF cells formed are of spherical and polyhedral shapes, and the cell size increased with decrease in the density of the RPUF samples. Foaming and the formation of cell size and shape processes of RPUF samples can be explained by nucleation and growth mechanism. Blowing gas is formed by the reaction of isocyanate and water as well as by the evaporation of physical blowing agent such as methylene chloride utilizing the reaction heat of polyol and isocyanate. Exothermic reac-

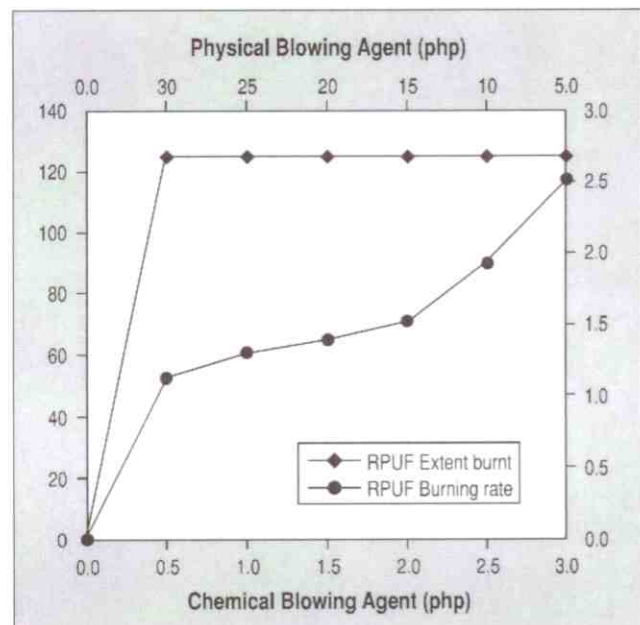


Figure 1. The variations of extent burnt rate and burning rate of the RPUF samples blown with various combinations of chemical blowing agents.

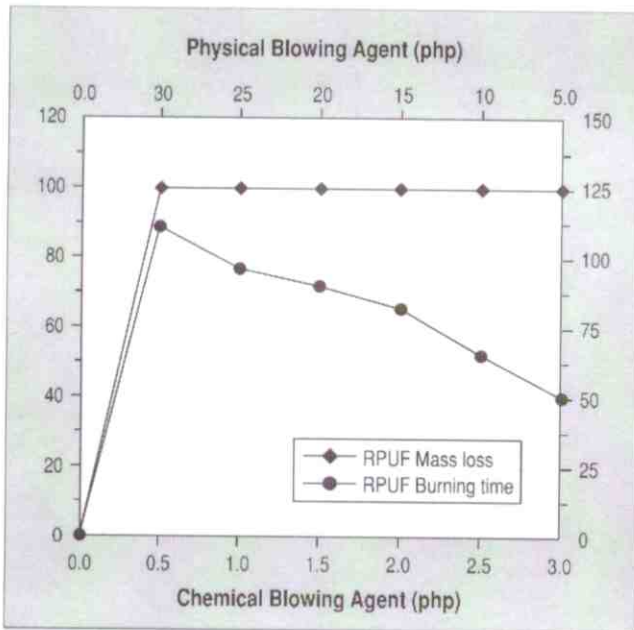


Figure 2. The variations of percent mass loss (PML) and burning time of the RPUF samples blown with various combinations of chemical blowing agents.

tion of polyol and isocyanate causes the supersaturation of the reactive mixture, resulting in the blowing gas being expelled from the reactive mixture and diffused into the nuclei. The diffusion of blowing gas into the nuclei begins the nucleation process. As a result, nuclei change to bubbles and bubble growth ends with unification of different sizes of bubbles. The unification of these bubbles forms the spherical shape. Spherical bubbles form the cells, which are separated by the cell membranes and change their shape to polyhedral.

During the foam formation, the reaction heat steadily raises the viscosity of the mixture until the foam has been cured and stabilized. The whole foam preparation process passes through the various physical and chemical phases.

The previous research work carried out and reported shows that during the foaming process the rate of nucleation was smaller with a physical blowing agent and larger with a chemical blowing agent at a higher initial blowing agent concentration. As a result, the average bubble diameter was changed with the initial blowing agent concentrations.

However, the cell size and shape did not significantly change with the type of blowing agent. The cell size of the RPUF sample blown by either chemical or physical blowing agent increased with the increase in the blowing agent concentration. The increase in the size of the RPUF cells may be due to the coalescence of the RPUF cells. Thus cell size of the RPUF samples blown by chemical blowing agent increased from 162 to 278 μm with an increase in blowing agent content from 0.5 to 3.0 php, respectively. This is due to the fact that the increase of chemical blowing agent content generates more bubbles, and increased bubbles combine with each other. Therefore, the cell size of the RPUF sample increases with the increase of the chemical blowing agent content.

Flammability Characteristics

The flammability of RPUF depends on its composition and is closely related to the characteristics and quantity of chemical and physical blowing agents. Flammability characteristics of RPUF samples were mainly

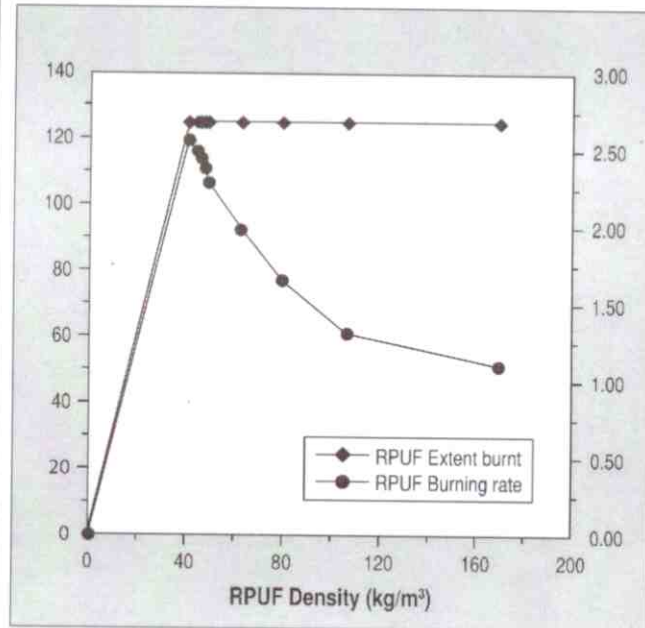


Figure 3. The flammability characteristics such as extent burnt and burning rate of RPUF samples of various densities.

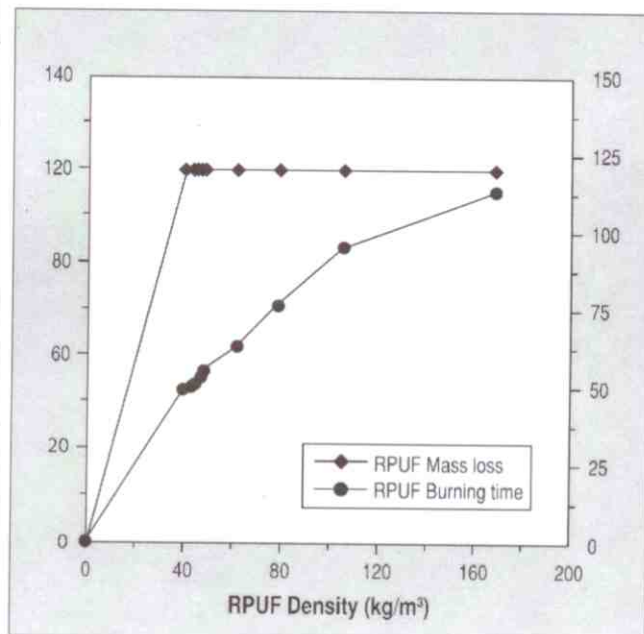


Figure 4. The flammability characteristics such as PML and burning time of RPUF samples of various densities.

measured from extent burnt, burning rate, percent mass loss (PML), and burning time obtained during the fire test. All these parameters are expressed in terms of average values. The variations of extent burnt rate, burning rate, PML, and burning time of the RPUF samples blown with various combinations of chemical and physical blowing agents are shown in Figures 1 and 2, respectively. Figure 1 presents the results, which show that by increasing the contents of chemical blowing agent from 0.5 to 3.0 php, in combination with decreasing contents of physical

blowing agent from 30 to 5, the extent burnt was unchanged; however, burning rate was increased from 1.13 to 2.52 mm/second.

As shown in Figure 2, with the similar combinations of chemical and physical blowing agents, PML was unchanged, whereas burning time was reduced from 111 to 50 seconds. These results reveal that increasing the contents of chemical blowing agent increases the burning rate, whereas increasing contents of physical blowing agent reduces the burning rate. As whole RPUF samples were consumed in fire, the extent burnt rate and PML were unchanged. Thus, RPUF samples blown by a chlorinated physical blowing agent exhibit a lower flammability level due to the chlorine atoms located in the polymer structure than samples blown with a chemical blowing agent.

These results are quite consistent with the previous research work carried out and reported in the literature. The blowing agent content directly affects the density of RPUF. Density was found to be the key variable in controlling the flammability characteristics of RPUF. The flammability characteristics such as extent burnt rate and burning rate, PML, and burning time of RPUF samples of various densities are presented in Figures 3 and 4, respectively. These results show that as the density increased from 40.39 to 168.83 kg/m³, the extent burnt rate and PML were unchanged, whereas the burning rate was reduced from 2.56 to 1.10 mm/second and the burning time was increased from 49 to 113 seconds.

As the density of RPUF samples increases, the porosity and thickness of the skin layer of the samples decreased. Because of less porosity, RPUF samples take more time to burn, which results in a decrease in the burning rate. During fire exposure, the RPUF samples were burnt to their entire lengths, thus there was no change in the extent burnt rate

and PML. All the flammability characteristics results reveal that RPUF samples blown by physical blowing agent have lower flammability than the samples blown by chemical blowing agent. During flammability tests, burning time and burning rate of RPUF samples were affected greatly, whereas the extent burnt rate and PML remained unchanged.

Conclusions

RPUF samples were prepared from crude MDI, polyether polyol, amine catalyst, silicone surfactant, and 1, 4-butane diol. Water and methylene chloride were used as chemical and physical blowing agents respectively.

The density of RPUF samples blown by mixture of chemical and physical blowing agents was decreased sharply when the contents of chemical and physical blowing agents were used individually.

The results of morphology demonstrate that the cell size of the RPUF samples increased with an increase in chemical and physical blowing agent contents. The cell size of RPUF samples blown by physical blowing agent and mixture of chemical and physical blowing agents exhibits behavior almost similar to the behavior of the RPUF samples blown by only chemical blowing agent.

The study reveals that the content of chemical and physical blowing agents, and so the density, influences the flammability characteristics of RPUF. RPUF samples blown by physical blowing agent exhibit lower flammability than the samples blown by chemical blowing agent. The blowing agent contents, and increase in the density, affect mainly the burning time and burning rate, whereas no change was observed in the extent burnt rate and the PML of the RPUF samples. ●

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