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Density, Cell Morphology and Flammability Characteristics of Rigid Polyurethane Foam Blown with Chemical and Physical Blowing Agents

Harpal Singh[1] & A. K. Jain[2]

Fire Research Laboratory, Central Building Research Institute, Roorkee-247667, India
[2]Department of Chemistry, Indian Institute of Technology, Roorkee-247667, India

ABSTRACT

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 was ranged from 240.1 to 33.4 kg/m^3 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 mm 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

Polyurethane had attracted the attention of researchers in the year 1849 when Wurtzdhk Hoffman of Germany reported the reaction of the hydroxyl compound with an isocyanate. Otto Bayer had studied the commercial development of polyurethane in 1937 but Rinkie and collaborators found its commercial use in 1938. The commercial production of polyurethane foams was started in the year 1954 [1]. A polymer containing a functional group of urethane (-NHCOO-) is called polyurethane. Structurally polyurethane is extremely large and complex polymer which 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 (RPUFs) 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 [2]. Some typical engineering applications of RPUF are in the field of transportation, refrigeration technology and appliances, building construction industry, automotive industry, packaging, carpet underlay and sporting goods [3-4]. RPUF is prepared by mixing polyol with catalyst, surfactant, chain extender, chemical and physical blowing agents in the first stage. In the second stage blended polyol is mixed with diisocyanate to react. During mixing some air bubbles are introduced into the mixture and they serve as nuclei for foam cells. The nuclei turned into the bubbles are stabilized by silicone surfactant [2, 5]. The foaming of the RPUF can be carried out either by chemical blowing agent or physical blowing agent or by the mixture of chemical and physical blowing agents. Water is one of the most widely used as chemical blowing agent. Water 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 into 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 hydro chlorofluorocarbons (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 the branching and cross-linking in the RPUF structure by forming allophanate and biuret respectively [2-4].

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 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.

EXPERIMENTAL

Materials

The materials and chemicals were obtained from branded and commercial sources. Crude 4, 4'-diphenylmethane diisocyanate (CMDI) and polyether polyol were obtained from Industrial Foams Ltd. (Delhi, India). 1, 4-butane diol, methylene chloride, stannous octoate (stannous 2-ethyl hexanoate) and triethylene diamine [1, 4 diazabicyclo (2, 2, 2) octane] were obtained from Spectrochem Pvt. Ltd. (Mumbai, India), E. Merck Ltd. (Mumbai, India), Sigma Chemicals Co. (St. Louis, USA) and Fluka chemie GmbH (Steinheim, Germany) respectively. Prior to the addition into the formulation, amine catalyst was not dissolved in any medium and was 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.

RPUF FORMULATION

Formulation of rigid polyurethane foam (RPUF) is basically 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 [3]. The amount of amine catalyst, mixture of amine and tin catalysts and water were varied 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 carried out a series of foam preparation experiments. The amount of 1, 4-butane diol can be varied depending upon the requirement of hard segment and cross-linking into the foam structure [6].

RPUF SAMPLE PREPARATION

RPUF samples with different amount (php) of ingredients were prepared through one-shot method [3-4]. Except 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. Then CMDI was added into the blended polyol and mixed for 20 seconds under overhead electric stirrer. The stirrer speed was set at 3000 rpm throughout the mixing. After mixing, the reactants were discharged into an open mould

(200´200´250 mm) lined with paper to produce free-rise foam. As the reactants mixture was poured into the mould, 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. Number, size and distribution of the nuclei determine the final foam structure [7]. The foam cake was then cured for 48 hours at room temperature. Although foam can also be cured at elevated temperatures, however we preferred to perform the curing at room temperature to observe the foam properties at ambient processing conditions.

The effect on RPUF densities blown by chemical, physical and mixture 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 to 3.0 php with an increment of 0.5 php. Similarly the amount of methylene chloride varied from 0 to 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 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 resulted into a cellular structure. Similarly methylene chloride when used as blowing agent, it boils and evaporates by the heat generated through exothermic reaction of CMDI and polyether polyol and inflates the reactants. Tables 1 and 2 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/

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	0.6	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

[a]Parts by 100 parts of polyether polyol
[b]W-MC denotes the amount of chemical blowing agent – physical blowing agent

Sample codes (RPUF-W-MC)	P olyether 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-W-0.0	100	180.6	0.6	20	1.0	0.5	5_30[b]
RPUF-W-0.0	100	188.4	0.6	20	1.0	1.0	5_30
RPUF-W-0.0	100	196.2	0.6	20	1.0	1.5	5-30
RPUF-W-0.0	100	204	0.6	20	1.0	2.0	5-30
RPUF-W-0.0	100	211.9	0.6	20	1.0	2.5	5-30
RPUF-W-0.0	100	219.7	0.6	20	1.0	3.0	5-30

[b] 0 – 30 parts of physical blowing agent with an increment of 5 parts

m^3. 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 15kv accelerating voltage to observe the shape and size of the cells. To define the cell size, measured cell sizes were averaged except 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 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. After complete fire exposure extent burnt, burning rate, percent mass loss (PML) and burning time of three specimens per sample were measured and averaged for analysis.

RESULTS AND DISCUSSION

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/m^3. The density of RPUF samples (RPUF-W) blown by chemical blowing agent was decreased from 240.1 to 56.5 kg/m^3, as the water content increased from 0 to 3.0 php respectively. The density of RPUF samples (RPUF-W) blown by chemical blowing agent is shown in Figure 1. The density of the RPUF samples blown by physical blowing agent (RPUF-MC) and by the mixture of chemical and physical blowing agents (RPUF-W-MC) is shown in Figure 2. As shown in Figure 2, the density of the RPUF samples blown by physical blowing agent decreased from 240.1 to 49.3 kg/m^3 as the content of physical blowing agent increased from 0 to 30 php, respectively. When 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/m^3.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 the four RPUF samples were scanned at the similar magnification in the free-rising direction. The micrographs of the RPUF samples blown by chemical blowing agent (0.5-0, 3.0-0) and physical blowing agent (0-5.0, 0-30) contents are shown in Figures 3 (a, b) and 4 (a, b) respectively. It is seen that 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 formation of cell size and shape processes of RPUF samples can be explained by nucleation and growth mechanism [8-9]. 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 reaction of polyol and isocyanate causes the super saturation 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 changes to bubble 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 [10]. The previous research work carried out and reported shows that during the foaming process the rate of nucleation was smaller with physical blowing agent and larger with 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 [9]. However, as shown in Figures 3 and 4, 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

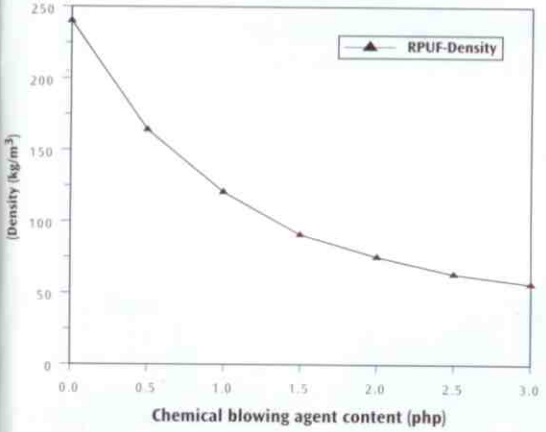

Figure 1. Density of the RPUF samples blown by chemical blowing agent (RPUF-W)

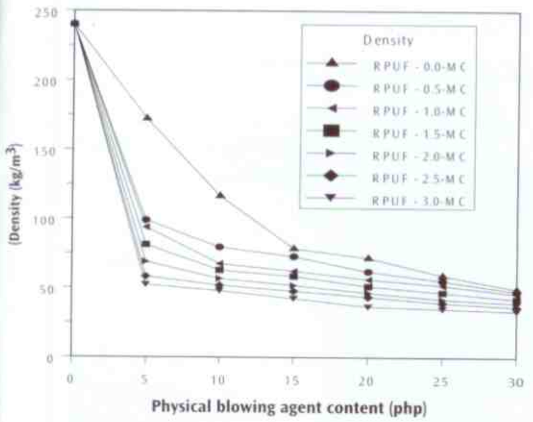

Figure 2. Density of the RPUF samples blown by physical blowing agent and mixture of chemical and physical blowing agents (RPUF-W-MC)

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 mm to 278 mm 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.

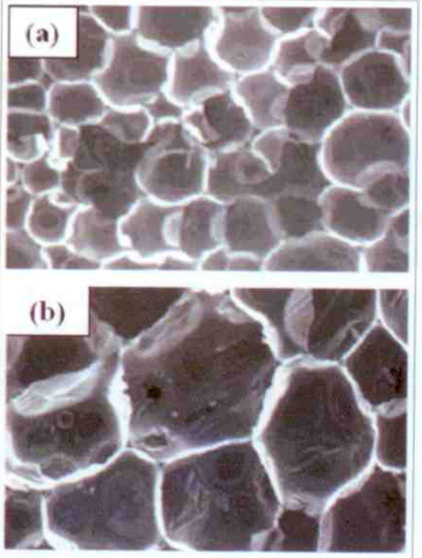

Figure 3. Scanning electron micrographs of RPUF samples blown with chemical blowing agent: (a) RPUF-0.5-0 (density 56.5 kg/m³) and (b) RPUF-3.0-0 (density 164.2 kg/m³)

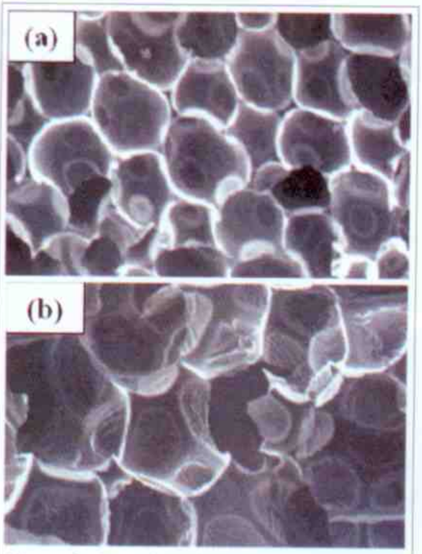

Figure 4. Scanning electron micrographs of RPUF samples blown with physical blowing agent: (a) RPUF-0-5.0 (density 49.3 kg/m³) and (b) RPUF-0-30 (density 172.2 kg/m³)

Flammability Characteristics

The flammability of RPUF depends on its composition and closely related to the characteristics and quantity of chemical and physical blowing agents [11]. Flammability characteristics of RPUF samples were mainly 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 and burning rate, PML and burning time of RPUF samples blown with various combinations of chemical and physical blowing agents are shown in Figures 5 and 6 respectively. Figure 5 presents the results which show that with an increasing contents of chemical blowing agent from 0.5 to 3.0, 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/s. As shown in Figure 6, with the similar combinations of chemical and physical blowing agents, PML was unchanged, whereas, burning time was reduced from 111 to 50s. These results reveal that increasing 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, thus extent burnt and PML were unchanged. Thus, RPUF samples blown by chlorinated physical blowing agent exhibit lower flammability level due to the chlorine atoms located in the polymer structure than samples blown with chemical blowing agent. These results are quite consistent with the previous research work carried out and reported in the literature [12-13]. 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 [14]. All the flammability characteristics results reveal that RPUF samples blown by physical blowing agent have lowered flammability than the samples blown by chemical blowing agent. During flammability test, burning time and burning rate of RPUF samples were affected greatly, whereas, extent burnt and PML were remain unchanged.

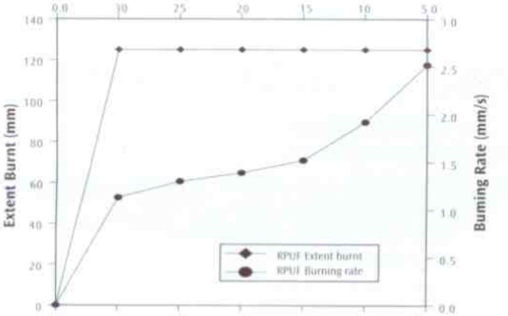

Figure 5. Extent burnt and burning rate of RPUF samples blown by chemical and physical blowing agents

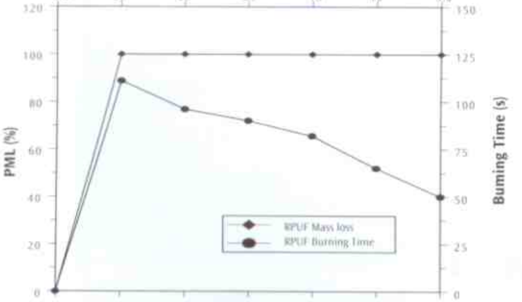

Figure 6. PML and burning time of RPUF samples blown by chemical and physical blowing agents

CONCLUSIONS

RPUF samples were prepared with crude MDI, polyether polyol, amine catalyst, silicone surfactant, 1, 4-butane diol with water and methylene chloride as blowing agents. 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 than the contents of chemical and physical blowing agent 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 influence the flammability characteristics of RPUF. RPUF samples blown by physical blowing agent exhibit lowered flammability than the samples blown by chemical blowing agent. The blowing agent contents and increase in the density affects mainly the burning time and burning rate, whereas, no change was observed in extent burnt and PML of the RPUF samples.

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