Reactivity of the Raw Materials and Their Effects on the Structure and Properties of Rigid Polyurethane Foams

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ABSTRACT: Formulations for rigid polyurethane foams (RPUFs) based on crude 4,4′-diphenylmethane diisocyanate, polyether polyol, triethylenediamine, 1,4-butane diol, poly(siloxane ether), methylene chloride, and water were studied. The stoichiometric ratios of various foam ingredients and their effects on physical properties such as the cream time, gel time, tack-free time, and density of the RPUF samples were studied. The results indicated that the rate of RPUF formation increased with the catalyst (triethylenediamine and tin) and water content. The density of the RPUF samples blown with water, methylene chloride, and a mixture of water and methylene chloride decreased from 240.1 to 33.4 kg/m^3 with an increase in the blowing agent contents. However, the RPUF density increased with increasing contents of 1,4-butane diol. The cell morphology and thermal properties of the RPUF samples were investi-

gated with scanning electron microscopy, thermogravimetric analysis, derivative thermogravimetry, and differential thermal analysis. Scanning electron microscopy results revealed an average increase in the cell size of the RPUF samples from 162 to 278 μm with increased water content. A thermal behavior study indicated that the RPUF samples decomposed in nitrogen and degraded in air through two and three weight-loss stages, respectively. Foam pyrolysis in nitrogen and combustion in air led to 15 and 0% char residue, respectively. The results indicated that the thermal stability of the RPUFs was better in nitrogen than in an air atmosphere. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1014–1023, 2007

Key words: blending; blowing agents; morphology; polyurethanes; pyrolysis

INTRODUCTION

Polyurethane attracted the attention of researchers in 1849 when Wurtzdhk Hoffman of Germany reported the reaction of the hydroxyl compound with an isocyanate. Otto Bayer studied the commercial development of polyurethane in 1937, but Rinkie and his collaborators discovered its commercial use in 1938. The commercial production of polyurethane foams was started in 1954.[1] A polymer containing a functional group of urethane (—NHCOO—) is called polyurethane. 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 urethane linkages. Depending on the ingredients and composition, polyurethane can be used for the 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 a closed cell. Closed-cell foams are

generally rigid in nature and are most suitable for thermal insulation because of their low thermal conductivity, low density, high strength-to-weight ratio, and low moisture permeability.[2] Some typical engineering applications of RPUFs are in transportation, refrigeration technology and appliances, building construction, the automotive industry, packaging, carpet underlayers, and sporting goods.[3,4]

RPUFs are prepared through the mixing of a polyol with water, a catalyst, a surfactant, a chain extender, and a physical blowing agent in the first stage. In the second stage, the blended polyol is mixed with a diisocyanate to react. During the mixing, some air bubbles are introduced into the mixture, and they serve as nuclei for foam cells. The nuclei, turned into bubbles, are stabilized by a silicone surfactant.[2,5] The foaming of RPUFs can be carried out with a chemical blowing agent, a physical blowing agent, or a mixture of chemical and physical blowing agents. Water is one of the most widely used chemical blowing agents. Water reacts with a diisocyanate and produces unstable carbamic acid initially, which immediately decomposes into an amine and carbon dioxide. This carbon dioxide diffuses into the already present air bubbles, and this results in a rise in the foam due to the increase in

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the bubble size. At the same time, the viscosity of the medium increases because of polymerization and gelation. The widely used physical blowing agents are chlorofluorocarbons and hydrochlorofluorocarbons. RPUF formation is principally based on the reaction of a polyol with a diisocyanate. The reaction is exothermic, and the heat of the reaction is used to form a cellular structure by the evaporation of the physical blowing agent. Isocyanate–urethane and isocyanate–urea reactions lead to branching and crosslinking in the RPUF structure by forming allophanate and biuret, respectively.[2–4]

The kinetic rate of reactions of RPUF formation mainly depends on the rates of the blowing and gelling reaction. The kinetic rates of these two reactions are controlled by an amine catalyst, a tin catalyst, or a combination of the two. The rate of foam formation is also affected by a higher ratio of NCO to OH or an increase in the temperature of the ingredients. Thus, RPUF formation is influenced by the quantity of the catalyst, the contents of the diisocyanate and polyol, and the temperature of the ingredients.[2]

This study deals with the composition, preparation, and reactivity of various RPUF ingredients. The effects of the chemical blowing agent, physical blowing agent, a mixture of chemical and physical blowing agents, an amine catalyst, a mixture of amine and tin catalysts, a chain extender, and a surfactant on the physical and morphological properties of RPUF samples were investigated. The thermal behavior of the prepared RPUFs was also studied. An economically efficient and suitable chemical composition for the preparation of RPUFs and an investigation of the reactivity and effects of various ingredients on the foam structure and properties were the main objectives of this research. RPUFs were prepared from crude 4,4′-diphenylmethane diisocyanate (CMDI) with a functionality of 2.2 and from polyether polyol with a functionality of 4.3 and a hydroxyl value of 440. CMDI and polyether polyol had a major impact on the properties of the RPUFs. Triethylenediamine (TED), stannous octoate, 1,4-butane diol, and poly(siloxane ether) were used as an amine catalyst, a tin catalyst, a chain extender, and a surfactant, respectively, during the RPUF preparation. Water as a chemical blowing agent and methylene chloride as a physical blowing agent were used. The reactivity of the raw materials was studied through the variation of the quantities of the amine catalyst, mixture of the amine and tin catalysts, 1,4-butane diol, poly(siloxane ether), and water during the preparation of the RPUF samples. Through the variation of the compositions and amounts of water, methylene chloride, and a mixture of water and methylene chloride, RPUF samples of various densities were obtained. Physical properties such as the cream time, gel time, tack-free time, and density of the RPUF samples were studied. The morphological properties and thermal behavior in air and nitrogen atmospheres of RPUF samples were also studied with scanning electron microscopy (SEM), thermogravimetric analysis (TGA), derivative thermogravimetry (DTG), and differential thermal analysis (DTA).

EXPERIMENTAL

Materials

The materials and chemicals were obtained from branded and commercial sources. 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 TED [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, MO), and Fluka Chemie GmbH (Steinheim, Germany), respectively. Before the addition to the formulation, the amine catalyst was not dissolved in any medium and was used as such. Poly(siloxane ether) was obtained from Sheela Foams Pvt., Ltd. (Ghaziabad, India), and Industrial Foams. Ordinary water was used as a chemical blowing agent. The chemicals were used as received. Some of the physical characteristics of the chemicals are shown in Table I.

TABLE I
Physical Characteristics of the Chemicals[a]

Chemicals	Functionality	Equivalent weight (g/mol)	Comments
CMDI	2.2	134.0	NCO concentration = 31.32%
Polyether polyol	4.3	127.5	OH value = 440 mg of KOH/g
TED	—	—	Blowing catalyst
Stannous octoate	—	—	Gelling catalyst
Water	2.0	9.0	Chemical blowing agent
Poly(siloxane ether)	—	—	Silicone surfactant
1,4-Butane diol	2.0	45.1	Chain extender
Methylene chloride	—	—	Physical blowing agent

[a] Provided by the suppliers and manufacturers.

RPUF formulations

The RPUF formulations were basically based on poly-ether polyol, CMDI, TED, poly(siloxane 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 a 5% weight excess of CMDI was used for the completion of the reaction. This 5% weight excess of CMDI was calculated from the isocyanate index (NCO/OH = 1.05), which was based on the number of equivalents of diisocyanate, polyether polyol, and water.[3] The amounts of the amine catalyst, the mixture of the amine and tin catalysts, and water were varied to obtain the desired cream times, gel times, and tack-free times. The amounts of water and methylene chloride were varied and calculated to obtain the desired foam densities. The amounts of TED, poly(siloxane ether), 1,4-butane diol, water, and methylene chloride [parts per 100 parts of polyether polyol by weight (php)] were selected to be optimal after a series of foam preparation experiments were carried out. The amount of 1,4-butane diol could be varied, depending on the requirements for the hard segment and crosslinking into the foam structure.[6] The basic formulation used for the RPUF preparation is presented in Table II.

RPUF sample preparation

RPUF samples with different amounts (php) of the ingredients were prepared through a one-shot method.[3,4] Except for CMDI, all the raw chemicals, such as TED, poly(siloxane ether), 1,4-butane diol, water, and methylene chloride, were first manually well blended with polyether polyol for 30 s in a stainless steel beaker. Then, CMDI was added to the blended polyol and mixed for 20 s under an overhead electric stirrer. The stirrer speed was set at 3000 rpm throughout the mixing. After the mixing,
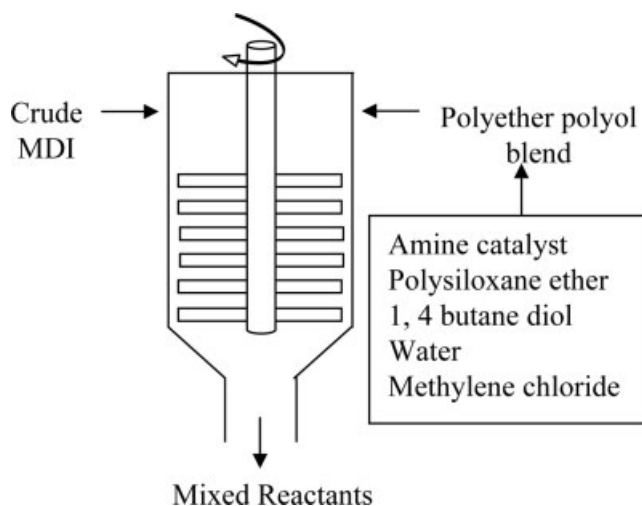
TABLE II
Chemical Formulations of RPUFs

Ingredients	Amount
Polyether polyol	100.00 php
TED	0–0.9 php[a]
Water	0–3.0 php[b]
Poly(siloxane ether)	0–2.0 php[c]
1,4-Butane diol	0–30 php[d]
Methylene chloride	0–30 php[e]
CMDI	Stoichiometric + 5%

[a] With an increment of 0.1 parts.
[b] With an increment of 0.5 parts.
[c] With an increment of 0.25 parts.
[d] With an increment of 2.5 or 5.0 parts.
[e] With an increment of 5.0 parts.

Figure 1 Blending and mixing process for the RPUF ingredients.

the reactants were discharged into an open mold (200 × 200 × 250 mm³) lined with paper to produce a free-rise foam. As the reactant mixture was poured into the mold, the formation of many very small bubbles was observed, and they 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 determined the final foam structure.[7] The foam cake was then cured for 48 h at room temperature. Although foams can also be cured at elevated temperatures, we preferred to perform the curing at room temperature to observe the foam properties under the ambient processing conditions. The charging and mixing of all the foam ingredients inside the stirrer are illustrated in Figure 1.

The kinetic rate of RPUF formation was investigated with an amine catalyst and a mixture of amine and tin catalysts. The amount of the amine catalyst was varied from 0 to 0.9 php with an increment of 0.1 php. Similarly, the amount of the tin catalyst was also varied from 0 to 0.10 php with an increment of 0.025 php in combination with 0.6 php of the amine catalyst. The amounts of poly(siloxane ether), 1,4-butane diol, water, and methylene chloride were fixed at 1.0, 20, 3.0, and 5.0 php. The amount of CMDI required for the formulation was 219.7 parts by weight. This 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, a 5% excess (NCO/OH = 1.05) of CMDI was used. The chemical compositions of the RPUF samples (RPUF–A–T) with an amine catalyst and a mixture of amine and tin catalysts are shown in Table III. In the sample code, A and T denote the amounts of the amine and tin catalysts, respectively.

TABLE III
Chemical Compositions of RPUF–A–T Samples with TED and Stannous Octoate Catalysts

Sample	Polyether polyol (php)	CMDI (php)	TED (php)	Tin (php)	1,4-Butane diol (php)	Poly(siloxane ether) (php)	Water (php)	Methylene chloride (php)
RPUF–0–0.0	100	219.7	0.0	0.0	20	1.0	3.0	5.0
RPUF–A–0.0	100	219.7	0.1	0.0	20	1.0	3.0	5.0
RPUF–A–0.0	100	219.7	0.2	0.0	20	1.0	3.0	5.0
RPUF–A–0.0	100	219.7	0.3	0.0	20	1.0	3.0	5.0
RPUF–A–0.0	100	219.7	0.4	0.0	20	1.0	3.0	5.0
RPUF–A–0.0	100	219.7	0.5	0.0	20	1.0	3.0	5.0
RPUF–A–0.0	100	219.7	0.6	0.0	20	1.0	3.0	5.0
RPUF–A–0.0	100	219.7	0.7	0.0	20	1.0	3.0	5.0
RPUF–A–0.0	100	219.7	0.8	0.0	20	1.0	3.0	5.0
RPUF–A–0.0	100	219.7	0.9	0.0	20	1.0	3.0	5.0
RPUF–0.6–T	100	219.7	0.6	0.025	20	1.0	3.0	5.0
RPUF–0.6–T	100	219.7	0.6	0.050	20	1.0	3.0	5.0
RPUF–0.6–T	100	219.7	0.6	0.075	20	1.0	3.0	5.0
RPUF–0.6–T	100	219.7	0.6	0.100	20	1.0	3.0	5.0

The effect of the chain extender on the RPUF properties was studied through the variation of the amount of 1,4-butane diol from 0 to 30 php with increments of 2.5 and 5.0 php. The amounts of poly(siloxane ether), TED, water, and methylene chloride were fixed at 1.0, 0.6, 3.0, and 5.0 php. The amount of CMDI depended on the various amounts of 1,4-butane diol and other reactive ingredients. To investigate the effect of the surfactant contents on the properties of the RPUF samples, the amount of poly(siloxane ether) was varied from 0 to 2.0 php with an increment of 0.25 php. The amounts of CMDI, TED, 1,4-butane diol, water, and methylene chloride were fixed at 219.7, 0.6, 20, 3.0, and 5.0 php. The chemical compositions of the RPUF samples (RPUF–

BD–S) with 1,4-butane diol and poly(siloxane ether) are shown in Table IV. In the sample code, BD and S represent the amounts of the chain extender and surfactant, respectively.

The effect on the properties of RPUFs blown with chemical, physical, and both chemical and physical blowing agents was investigated through the variation of the amounts of water and methylene chloride. 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 was varied from 0 to 30 php with an increment of 5 php. The mixture of water and methylene chloride was also used through the variation of the amount of one blowing agent, whereas the amount of the other blowing agent was

TABLE IV
Chemical Compositions of RPUF–BD–S Samples with 1,4-Butane Diol and Poly(siloxane ether)

Sample	Polyether polyol (php)	CMDI (php)	TED (php)	1,4-Butane diol (php)	Poly(siloxane ether) (php)	Water (php)	Methylene chloride (php)
RPUF–0.0–1.0	100	157.2	0.6	0.0	1.00	3.0	5.0
RPUF–BD–1.0	100	165	0.6	2.5	1.00	3.0	5.0
RPUF–BD–1.0	100	172.8	0.6	5.0	1.00	3.0	5.0
RPUF–BD–1.0	100	180.6	0.6	7.5	1.00	3.0	5.0
RPUF–BD–1.0	100	188.4	0.6	10	1.00	3.0	5.0
RPUF–BD–1.0	100	196.3	0.6	12.5	1.00	3.0	5.0
RPUF–BD–1.0	100	204.1	0.6	15	1.00	3.0	5.0
RPUF–BD–1.0	100	219.7	0.6	20	1.00	3.0	5.0
RPUF–BD–1.0	100	235.3	0.6	25	1.00	3.0	5.0
RPUF–BD–1.0	100	250.9	0.6	30	1.00	3.0	5.0
RPUF–20–0.0	100	219.7	0.6	20	0.00	3.0	5.0
RPUF–20–S	100	219.7	0.6	20	0.25	3.0	5.0
RPUF–20–S	100	219.7	0.6	20	0.50	3.0	5.0
RPUF–20–S	100	219.7	0.6	20	0.75	3.0	5.0
RPUF–20–S	100	219.7	0.6	20	1.00	3.0	5.0
RPUF–20–S	100	219.7	0.6	20	1.25	3.0	5.0
RPUF–20–S	100	219.7	0.6	20	1.50	3.0	5.0
RPUF–20–S	100	219.7	0.6	20	1.75	3.0	5.0
RPUF–20–S	100	219.7	0.6	20	2.00	3.0	5.0

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TABLE V
Chemical Compositions of RPUF–W–MC Samples Blown with Water and Methylene Chloride

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Sample	Polyether polyol (php)	CMDI (php)	TED (php)	1,4-Butane diol (php)	Poly(siloxane ether) (php)	Water (php)	Methylene chloride (php)
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

constant, and vice versa. The amounts of TED, poly (siloxane ether), and 1,4-butane diol were fixed at 0.6, 1.0, and 20 php. The amount of CMDI required for the reaction with various amounts of water and other reactive ingredients was calculated from their equivalent weights. When water was used as the blowing agent, it reacted with CMDI to produce disubstituted urea and carbon dioxide. The carbon dioxide inflated the reactants, and this resulted in a cellular structure. Similarly, methylene chloride when used as a blowing agent, boiled and evaporated because of the heat generated through the exothermic reaction of CMDI and polyether polyol and inflated the reactants. Tables V and VI show the chemical compositions of RPUF samples blown with water, methylene chloride, and a mixture of water and methylene chloride (RPUF–W–MC). In the sample codes, W and MC denote the amounts of water and methylene chloride used, respectively.

Measurements

The kinetic rate of RPUF formation mainly depended on some of the physical properties, such as the cream time, gel time, and tack-free time.[8] The cream time was the beginning point of the foam rise. At this point, the mixed reactants changed color from dark brown to a lighter color because of the evolution of the blowing agent. The gel time was the starting point of the stable-shape polymer network formation through the urethane and urea linkages and crosslinking and branching reactions of allophanate and biuret, respectively. The tack-free time was the time at which the outer surface of the foam lost its stickiness and the perfectly crosslinked RPUF was removed from the mold. These properties were measured with a digital stopwatch timer device during the RPUF sample preparation. The density of the RPUF samples was measured according to ASTM D 1622. The size (length × width × thickness) of the specimens was 30 × 30 × 30 mm, respectively. The RPUF specimens were conditioned at 25°C and 55% relative humidity for 48 h before their density measurements. The densities of five specimens per sample were measured and averaged.

The morphology of the RPUF samples was observed with a Leo (Cambridge, UK) 438 VP scanning electron microscope. The samples were cryogenically fractured, gold-coated, and scanned at a

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TABLE VI
Chemical Compositions of RPUF–W–MC Samples Blown with a Water and Methylene Chloride Mixture

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Sample	Polyether polyol (php)	CMDI (php)	TED (php)	1,4-Butane diol (php)	Poly(siloxane ether) (php)	Water (php)	Methylene chloride (php)
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	0.6	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

[a] 0–30 parts of methylene chloride with an increment of 5 parts.

15-kV accelerating voltage to observe the shapes and sizes of the cells. To define the cell size, the measured cell sizes were averaged, except for the sizes for the largest and smallest cells. The thermal properties of the powdered RPUF samples were measured on a TGA/DTG/DTA apparatus (Pyris Diamond, PerkinElmer, Shelton, CT). A platinum pan was used to place the sample powder inside the heating chamber, and the samples were heated up to 1000°C for 100 min at a rate of 10°C/min under both air and nitrogen atmospheres.

RESULTS AND DISCUSSION

Kinetic rate of RPUF formation

The kinetic rate of RPUF formation was mainly measured from the cream time, gel time, and tack-free time. The gelling (isocyanate–hydroxyl) and blowing (isocyanate–water) reactions were controlled by tin and amine catalysts, respectively.[2,7] Figure 2 shows that an increasing amount of the amine catalyst reduced the cream time, gel time, and tack-free time from 110, 210, and 540 s to 18, 85, and 120 s, respectively. Similarly, Figure 3 shows that a mixture of the amine and tin catalysts reduced the cream time, gel time, and tack-free time from 110, 210, and 540 s to 23, 53, and 89 s. In these results, the cream time was reduced with the amine catalyst, whereas the gel time and tack-free time were greatly affected in the presence of the tin catalyst. Figures 4 and 5 show that increasing contents of 1,4-butane diol and poly(siloxane ether) in the presence of the amine catalyst did not have any further effect on the cream time, gel time, and tack-free time. The results pre-
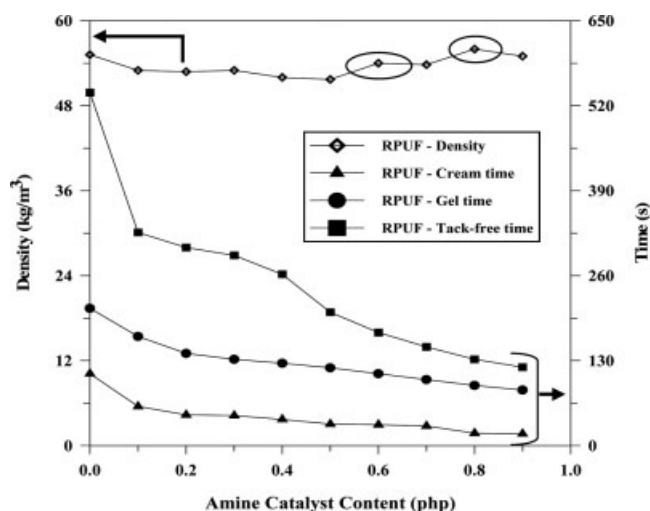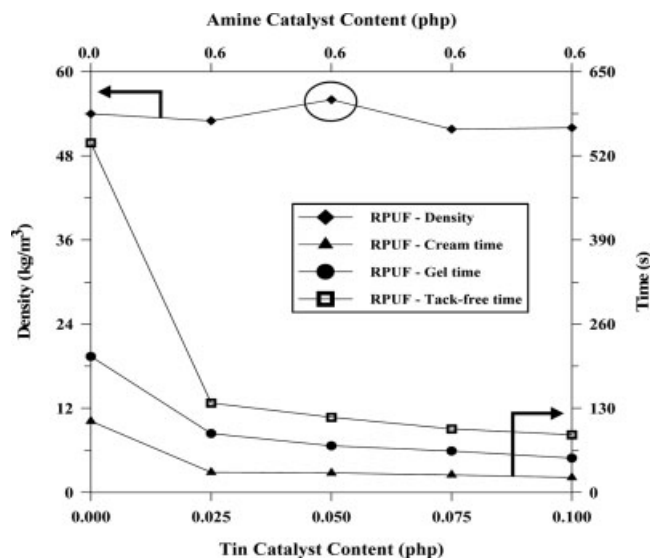

Figure 3 Effect of a stannous octoate and TED catalyst mixture on the density (the error is marked by a circle) and kinetic rate of the RPUF–T–A samples: (◆) density, (▲) cream time, (●) gel time, and (□) tack-free time.

sented in Figure 6 show that the cream time, gel time, and tack-free time were also reduced with increasing water content in the presence of the amine catalyst. Thus, the kinetic rate of RPUF formation increased with increasing contents of TED and a mixture of TED and stannous octoate catalysts. The TED catalyst mainly accelerated the blowing reaction, as confirmed by the faster cream time, and the stannous octoate catalyst only accelerated the gelling reaction, as confirmed by the faster gel time and tack-free time. The increasing contents of 1,4-butane
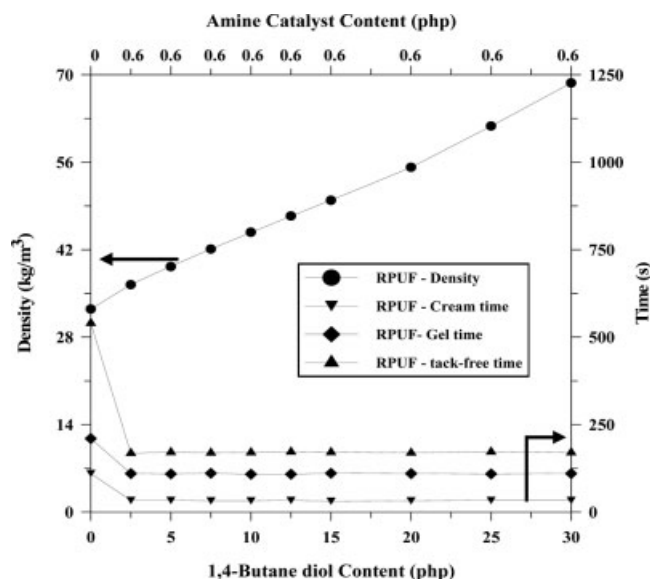

Figure 2 Effect of the TED catalyst on the density (the error is marked by circles) and kinetic rate of the RPUF–A samples: (◇) density, (▲) cream time, (●) gel time, and (■) tack-free time.

Figure 4 Effect of 1,4-butane diol on the density and kinetic rate of the RPUF–BD samples: (●) density, (▼) cream time, (◆) gel time, and (▲) tack-free time.
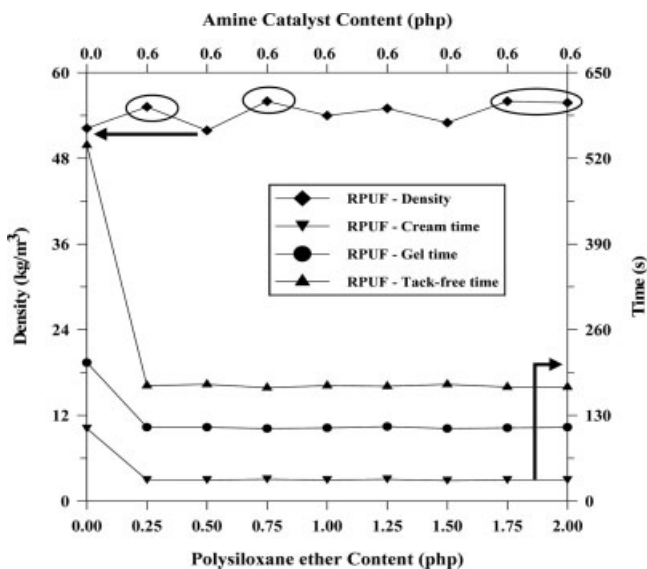
Figure 5 Effect of poly(siloxane ether) on the density (the error is marked by circles) and kinetic rate of the RPUF–S samples: (◆) density, (▼) cream time, (●) gel time, and (▲) tack-free time.

diol and poly(siloxane ether) did not have any influence on the kinetic rate of RPUF formation. The kinetic rate of RPUF formation also increased with an increase in the water content because the temperature of the reactants was increased by the heat exerted through the water–CMDI reaction.

Density measurements

The densities of the RPUF samples blown with and without a blowing agent and a mixture of blowing

agents were measured. The density of the RPUF samples in the absence of blowing agents was 240.1 kg/m^3. The density of the RPUF samples blown with water (RPUF–W) decreased from 240.1 to 56.5 kg/m^3 as the water content increased from 0 to 3.0 php. The densities of the RPUF–W samples are shown in Figure 6. The densities of the RPUF samples blown with methylene chloride (RPUF–MC) and by a mixture of water and methylene chloride (RPUF–W–MC) are shown in Figure 7. As shown in Figure 7, the density of the RPUF–MC samples decreased from 240.1 to 49.3 kg/m^3 as the content of methylene chloride increased from 0 to 30 php. When a mixture of water and methylene chloride was used as a blowing agent, the density of the RPUF–W–MC samples varied from 240.1 to 33.4 kg/m^3.

Furthermore, the density of the RPUF samples increased with the increasing content of 1,4-butane diol. When the 1,4-butane diol content was increased from 0 to 30 php, the density of the RPUF samples (RPUF–BD) increased from 32.5 to 68.7 kg/m^3. The densities of the RPUF–BD samples are shown in Figure 4. The effect of increasing the content of TED (RPUF–A), a mixture of stannous octoate and TED (RPUF–T–A), and poly(siloxane ether) (RPUF–S) on the RPUF density is shown in Figures 2, 3, and 5, respectively. As the amounts of TED, stannous octoate, and poly(siloxane ether) were increased, the density of the RPUF samples was affected only slightly. The slight variations in the density may have been due to the error involved during the experimental process. The error involved in the density measurement is marked by the circles in Figures 2, 3, and 5.
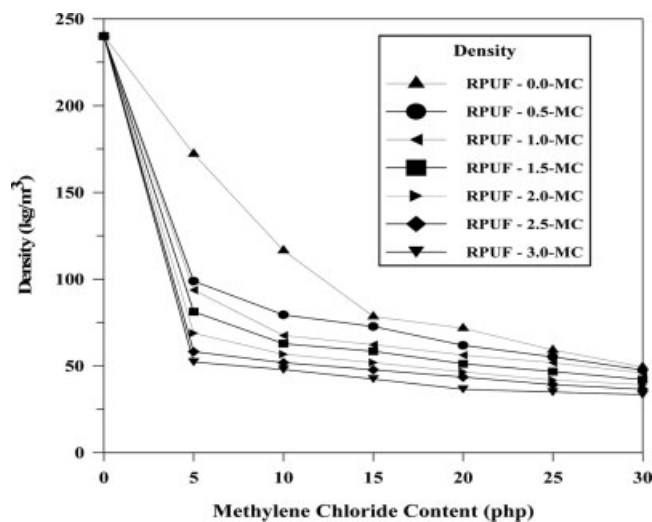

Figure 6 Density and kinetic rate of the RPUF–W samples: (◆) density, (▲) cream time, (●) gel time, and (▼) tack-free time.

Figure 7 Density of the RPUF–W–MC samples: (▲) RPUF–0.0–MC, (●) RPUF–0.5–MC, (◄) RPUF–1.0–MC, (■) RPUF–1.5–MC, (►) RPUF–2.0–MC, (◆) RPUF–2.5–MC, and (▼) RPUF–3.0–MC.
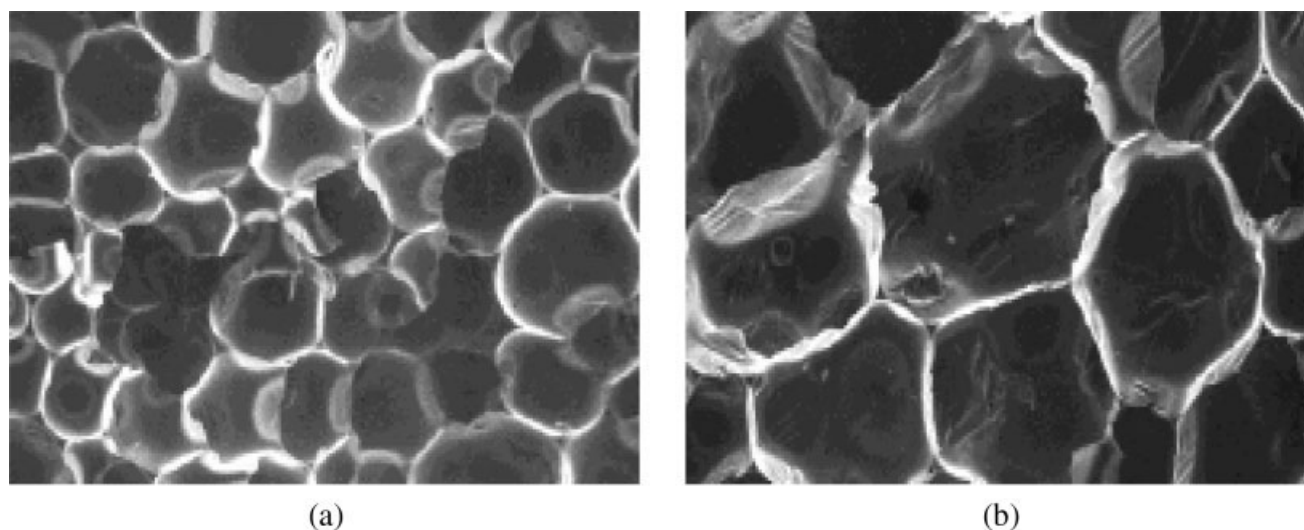
Figure 8 SEM micrographs of RPUF samples blown with water: (a) RPUF–0.5–0 (density = 56.5 kg/m^3) and (b) RPUF–3.0–0 (density = 164.2 kg/m^3).

Morphology

The cross-sectional surface of the RPUF samples individually blown with 0.5 php water (RPUF–0.5–0) and 3.0 php water (RPUF–3.0–0) and with 5 php methylene chloride (RPUF–0–5) and 30 php methylene chloride (RPUF–0–30) were observed under SEM. All four RPUF samples were scanned at a similar magnification in the free-rising direction. The micrographs of the RPUF samples blown with water (0.5–0 and 3.0–0) and methylene chloride (0–5.0 and 0–30) are shown in Figures 8(a,b) and 9(a,b), respectively. The RPUF cells that formed were spherical and polyhedral, and the cell size increased with a decrease in the density of the RPUF samples. The foaming and formation of the cell size and shape for

the RPUF samples can be explained by a nucleation and growth mechanism.[9,10] Blowing gas is formed by the reaction of isocyanate and water and by the evaporation of a physical blowing agent such as methylene chloride using the reaction heat of the polyol and isocyanate. An exothermic reaction of the 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 the blowing gas into the nuclei begins the nucleation process. As a result, the nuclei change into bubbles, and bubble growth ends with the unification of different sizes of bubbles. The unification of these bubbles forms the spherical shape. Spherical bubbles form the cells,
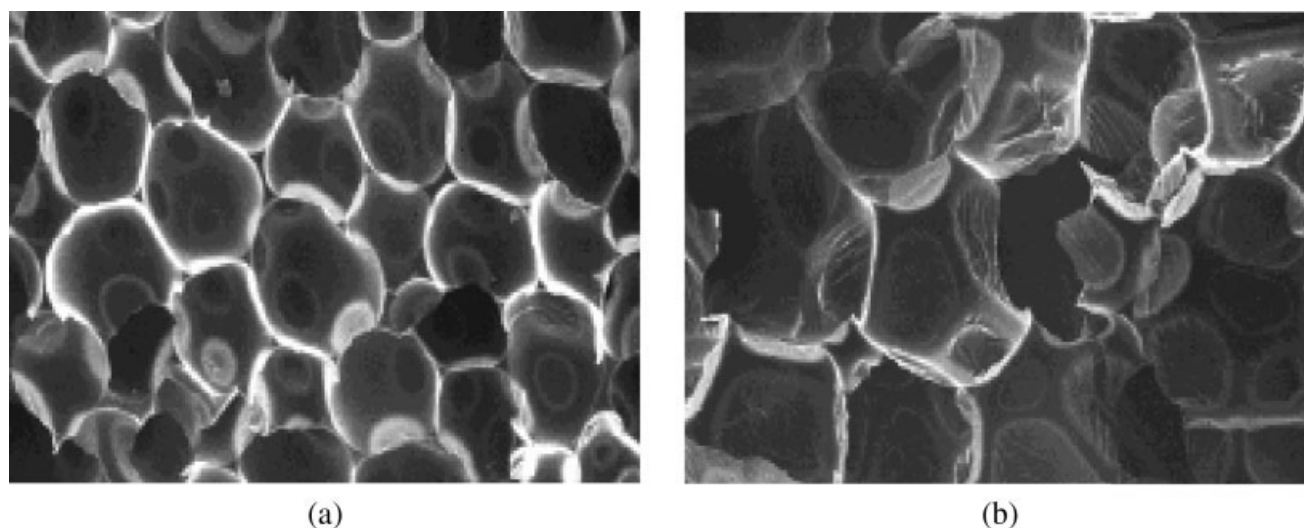

Figure 9 SEM micrographs of RPUF samples blown with methylene chloride: (a) RPUF–0–5.0 (density = 49.3 kg/m^3) and (b) RPUF–0–30 (density = 172.2 kg/m^3).
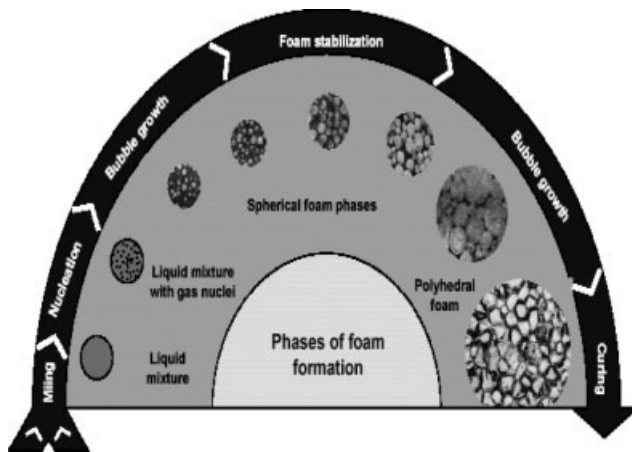
Figure 10 Different physical phases during RPUF formation.

which are separated by the cell membranes and become 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 various physical and chemical phases.[11] Some of the physical phases are illustrated in Figure 10. Niyogi et al.[10] reported 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, as shown in Figures 8 and 9, the cell size and shape did not significantly change with the type of blowing agent. The cell size of the RPUF samples blown with either water or methylene chloride increased with the increase in the blowing agent concentration. The increase in the size of the RPUF cells may have been due to the coalescence of the RPUF cells. Thus, the cell size of the RPUF samples

blown with water increased from 162 to 278 μm with an increase in the water content from 0.5 to 3.0 php. This is due to the fact that the increase in the water content generated more bubbles, and the increased number of bubbles combined with one another. Therefore, the cell size of the RPUF sample increased with the increase in the water content.

Thermal analysis

TG and DTG curves of RPUF samples in nitrogen and air are shown in Figure 11(a,b), respectively. The DTG curve of RPUF decomposition in nitrogen shows only two weight-loss stages, whereas the DTG curve in air indicates that three main weight-loss stages occur during degradation. This suggests that the RPUF degradation mechanism in air is much more complex than that in nitrogen.[12,13] In a nitrogen atmosphere, an RPUF sample does not show a distinct weight loss until the temperature rises to 225°C. During the first stage, the rate of weight loss begins to increase gradually to a maximum between 285 and 310°C through two successive decomposition processes. The minimum weight loss is observed during pyrolysis (second stage) after the sample is heated above 500°C, and this leads to an 11.5% char residue at 1000°C.

In an air atmosphere, the three weight-loss stages observed in the temperature regions of 216–337, 350–478, and 480–650°C are consistent with the findings of previous studies reported in the literature.[12,14–16] The rate of weight loss is minimum in the first and second stages and appears to increase gradually between 480 and 650°C, with a maximum at about 526°C during the third stage. The third stage, which has 0% char residue at 650°C, appears to be thermooxidative in nature because it does not exist in a nitrogen atmosphere.[12,13]
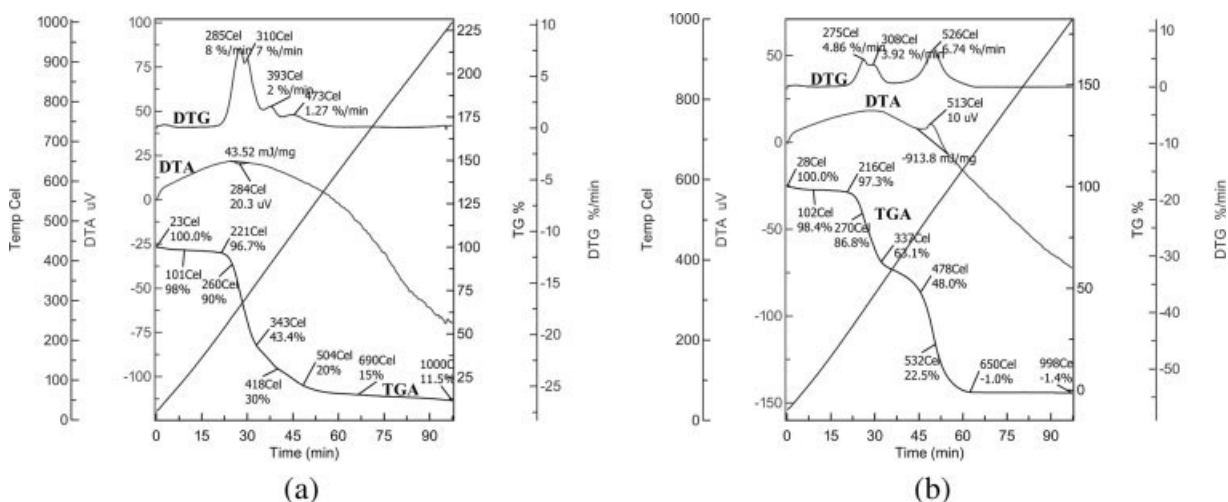

Figure 11 Thermograms of RPUF samples: (a) under nitrogen and (b) under air.

The thermal characteristics during the first and second stages appear to be similar in nitrogen and air through the initial decomposition temperatures, but the maximum decomposition temperature is higher in nitrogen than in air. This suggests that the first and second weight-loss stages in nitrogen have the same decomposition mechanism with degradation in air.[13] The thermal degradation kinetics suggest that the rate of weight loss is maximum during the first stage in nitrogen and slow in the first and second stages under an air atmosphere because of the decomposition, degradation, and pyrolysis.[13,17] However, the maximum weight loss occurs in the third stage in air because of combustion.[12,13] During combustion, oxygen reacts with the carbon of the charred residue to convert it into volatile carbon dioxide, and this results in no residue left behind at 650°C in air, whereas pyrolysis limits the development of volatile compounds, allowing 15% black char residue at 690°C in nitrogen. 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.[12,18]

CONCLUSIONS

RPUF samples were prepared with CMDI, polyether polyol, an amine catalyst, a silicone surfactant, 1,4-butane diol, and water and methylene chloride as blowing agents. The cream time, gel time, and tack-free time of the RPUF samples increased with the amine catalyst and the mixture of amine and tin catalysts. The mixture of amine and tin catalysts led to a faster cream time, gel time, and tack-free time than the catalysts individually. This was due to the synergistic effect between them. The cream time, gel time, and tack-free time of RPUFs also increased with an increase in the water content because of the heat of reaction exerted by the reaction of CMDI and water. The increasing contents of the silicone surfactant and chain extender did not have any effect on the cream time, gel time, and tack-free time of RPUF formation.

The densities of the RPUF samples blown with a mixture of water and methylene chloride decreased more sharply than the densities of the RPUF samples blown with water and methylene chloride individually. In contrast, the densities of the RPUF samples increased with increasing 1,4-butane diol content. The quantities of the amine, mixture of amine and tin catalysts, and poly(siloxane ether) showed negligible effects on the density of the RPUF samples. The morphology results demonstrated that the cell size of the RPUF samples increased with an increase in the water and methylene chloride contents. The cell size of the RPUF samples blown with methylene chloride and a mixture of water and methylene chloride exhibited behavior almost similar to the behavior of the RPUF samples blown with only water.

From the TG and DTG results, it could be seen that the foam samples decomposed in nitrogen and degraded in air through two and three weight-loss stages. The third stage in air was attributed to combustion, which disappeared in a nitrogen atmosphere. The onset degradation temperature was higher in nitrogen than in a air atmosphere. Foam decomposition in nitrogen and combustion in air during the first and third stages led to maximum weight loss, respectively. This resulted in 15 and 0% char residues in nitrogen and air atmospheres, respectively. On the basis of the thermal analysis data, it was concluded that the RPUF samples were more stable in nitrogen than in air.

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