Copper–Amine Complexes as New Catalysts for Rigid Polyurethane Foam Preparations

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ABSTRACT: A new class of catalyst for the preparation of rigid polyurethane (RPUR) foams was developed. Metal(II)–amine complexes [$M(en)_2$ and M(trien), where M = Cu or Ni, en = ethylenediamine, and trien = triethylenetetramine] were synthesized and used as catalysts in the preparation of RPUR foams. The catalytic activity of the metal(II)–amine complexes and properties of the RPUR foams were investigated and compared to those prepared by N,N-dimethylcyclohexylamine (DMCHA), which is a common commercial tertiary amine catalyst used in the preparation of RPUR foams. The use of $M(en)_2$ and M(trien) can improve the working environment in RPUR foam processing because DMCHA and other commercial tertiary amine catalysts have a strong odor, whereas $M(en)_2$ and M(trien) do not have any odor. The reaction times in RPUR foam preparation, namely, cream time, gel time, tack-free time, and rise time, were investigated. These data indicated that the copper–ethylenediamine complex [$Cu(en)_2$] and copper–triethylenetetramine complex [Cu(trien)] had comparable catalytic activity to DMCHA, whereas the catalytic activity of the nickel complexes was not good. Attenuated total reflection–IR spectroscopy of the RPUR foams prepared with $Cu(en)_2$ and Cu(trien) showed quantitative isocyanate (NCO) conversion. The density and compressive strength of the RPUR foams prepared from $Cu(en)_2$ and Cu(trien) were comparable to those prepared from DMCHA. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3520–3526, 2012

Key words: metal–organic catalysts/organometallic; polyurethanes; synthesis

INTRODUCTION

Rigid polyurethane (RPUR) foams are used in many applications, including as insulation material in refrigerators and packaging materials, because of their good mechanical properties and low thermal conductivity.[1] The main reactions that occur in the preparation of RPUR foam with water as a blowing agent are the reaction between isocyanate (NCO) groups in polymeric methylene diphenyl diisocyanate (PMDI) and hydroxyl groups in polyol to give urethane linkages (gelling reactions) and the reaction between NCO groups and water to release carbon dioxide (blowing reaction).

Organotin and tertiary amines are widely used as catalysts for RPUR foam preparation.[2] Examples are dibutyltin dilaurate, stannous octoate, N,N-dimethylcyclohexylamine (DMCHA), and 1,4-diazabicyclo[2.2.2]octane. The unfavorable properties of organotin and amine catalysts are their toxicity and strong odor, respectively. Tertiary amine emits odor in the working environment during the preparation of the foams when they are prepared on a large scale. Therefore, the development of alternative catalysts is always of interest. There are many works on the improvement of amine catalysts for polyurethane foam preparation.[3–7] Transition-metal complexes are being investigated with great interest as catalysts to replace organotin. For example, $M(acac)_n$ (where M = Mn, Fe, Co, Ni, or Cu) and tertiary amines have been used to catalyzed the reaction between hexamethylene diisocyante and diethylene glycol.[8] Other catalysts used for polyurethane formation have been metal complexes based on bismuth, zirconium, zinc, titanium, iron, and aluminum.[9–12] Copper(II)–amine complexes have been used as catalysts in the oxidative polymerization of phenol derivatives,[13–16] hydrolysis of organophosphate esters,[17] O-arylation reaction of phenols,[18] and epoxidation reaction.[19] For nickel(II)–amine complexes, they were employed as a catalyst for enecarbamate additions to butane-2,3-

dione[20] and as a catalyst for alkane hydroxylation with meta-chloroperoxybenzoic acid (*m*-CPBA).[21]

The objectives of this work was to synthesize metal–ethylenediamine complexes [M(en)$_2$'s] and metal–triethylenetetramine complexes [M(trien)'s], where M = Cu or Ni, and use them as catalysts for RPUR foam preparation. These metal–amine complexes could be easily prepared from inexpensive starting materials. They are odorless, and therefore, they offer another alternative option as RPUR foam catalysts. Their catalytic activities and the foam properties were compared with those obtained from DMCHA.

EXPERIMENTAL

Materials

Copper(II) acetate monohydrate [Cu(OAc)$_2$·H$_2$O], nickel(II) acetate tetrahydrate [Ni(OAc)$_2$·4H$_2$O], ethylenediamine (en), and triethylenetetramine (trien) were obtained from Aldrich, USA. PMDI (MR-200, % NCO = 31.0 wt %, average functionality = 2.7), polyol (Raypol 4221, sucrose-based polyether polyol, hydroxyl value = 440 mg of KOH/g, functionality = 4.3), polysiloxane surfactant (TEGOSTAB B8460), and DMCHA were supplied by South City Petrochem Co., Ltd. Distilled water was used as a blowing agent.

Measurements

Fourier transform infrared (FTIR) spectroscopy and attenuated total reflection (ATR)–IR spectra were recorded on a PerkinElmer RX I FTIR spectrometer and a Nicolet 6700 FTIR spectrometer, respectively, over the range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. Ultraviolet–visible (UV–vis) spectra were recorded on a Varian Cary 50 UV–vis spectrophotometer over the range 200–800 nm. Elemental analysis (CHN) was carried out with a PerkinElmer EP 2400 analyzer. The metal content was analyzed with a PerkinElmer AAnalyst 100 atomic absorption spectrometer. The density of the foams was measured according to ASTM D 1622-09; the size of specimen was 3.0 × 3.0 × 3.0 cm^3, and the average values of three samples are reported. Compression testing of the foams in parallel to the foam-rising direction was performed with a Lloyd LRX universal testing machine according to ASTM D 1621-09. For compression tests, the specimens were cut into a cubic shape with dimensions of 3.0 × 3.0 × 3.0 cm^3. The cross section of the specimens was 9.0 cm^2, which was less than that recommended by ASTM (25.8 cm^2). The rate of crosshead movement was fixed at 2.54 mm/min, and the preload cell used was 0.100 N. Thermogravimetric analysis (TGA) was performed with a Netzsch STA 409C thermogravimetric analyzer. All samples were heated from 25 to 600°C at a heating rate of 20°C/min under an N$_2$ atmosphere. The initial decomposition temperature was taken as the temperature where 5 wt % loss of the foam occurred. The morphology of the foams was studied with a Hitachi S-4800 scanning electron microscope. The samples were gold-coated before scanning, and the accelerating voltage was 20 kV.

Synthesis of the copper–ethylenediamine complex [Cu(en)$_2$]

The preparation of Cu(en)$_2$ was performed by the modification of a method reported in the literature.[22] A solution of en (0.42 mL, 6.28 mmol) was stirred in acetone (25 mL) at room temperature. Copper(II) acetate monohydrate (0.623 g, 3.12 mmol) was added to the en solution over a period of 10 min, and the reaction mixture was stirred at room temperature for 1 h. Cu(en)$_2$ precipitated from a blue solution, was subsequently isolated by filtration, and was dried *in vacuo* to remove acetone. Cu(en)$_2$ was obtained as a purple powder.

Yield = 0.618 g, 62%. IR (KBr, cm^{-1}): 3318, 3269, 3139 (N—H); 2986, 2953, 2884 (C—H); 1545 (asymmetric C=O, acetate); 1396 (symmetric C=O, acetate); 1326 (C—N); 1039 (C—O). UV: λ_{max}(MeOH) = 230 nm, molar absorptivity = 4790. ANAL. Calcd for CuC$_8$O$_4$H$_{22}$N$_4$·H$_2$O [Cu(en)$_2$(CH$_3$COO)$_2$·H$_2$O]: C, 30.04%; H, 7.56%; N, 17.52%; Cu, 21.05%. Found: C, 29.79%; H, 7.81%; N, 17.48%; Cu, 21.94%.

Synthesis of the nickel–ethylenediamine complex [Ni(en)$_2$]

Ni(en)$_2$ was synthesized with the same procedure used for Cu(en)$_2$. Ni(en)$_2$ was obtained as a purple red powder.

Yield = 0.682 g, 68%. IR (KBr, cm^{-1}): 3460, 3275 (NH stretching); 2946, 2944, 2890 (CH stretching); 1572 (asymmetric C=O stretching); 1408 (symmetric C=O stretching); 1333 (CN stretching); 1024 (CO stretching). ANAL. Calcd for NiC$_8$O$_4$H$_{22}$N$_4$ [Ni(en)$_2$(CH$_3$COO)$_2$]: C, 32.37%; H, 7.42%; N, 18.88%; Ni, 19.79%. Found: C, 32.37%; H, 7.42%; N, 17.73%; Ni, 19.80%.

Synthesis of the copper–triethylenetetramine complex [Cu(trien)]

The preparation of Cu(trien) was performed by modification of a method reported in the literature.[23] A solution of trien (0.43 mL, 2.89 mmol) in acetone (25 mL) was stirred at room temperature. Copper(II) acetate monohydrate (0.577 g, 2.89 mmol) was added to the trien solution over a period of 10 min. After

TABLE I
RPUR Foam Formulations (pbw)

Formulation (pbw)	NCO index	
	100	150
Polyol (Raypol 4221)	100	100
Catalysts (metal complexes)	1.0	1.0
Surfactant (TEGOTAB B8460)	2.5	2.5
Blowing agent (H$_2$O)	3.0	3.0
Polymeric MDI (MR-200)	151	227

the reaction mixture was stirred at room temperature for 1 h, the solution was evaporated and dried *in vacuo* to remove acetone. Cu(trien) was obtained as a blue viscous liquid.

Yield = 0.995 g, quantitative. IR (KBr, cm^{-1}): 3249 (N—H); 2954, 2887 (C—H); 1556 (asymmetric C=O, acetate); 1401 (symmetric C=O, acetate); 1339 (C—N); 1019 (C—O). UV: λ_{max}(MeOH) = 258 nm, molar absorptivity = 3480.

Synthesis of the nickel–triethylenetetramine complex [Ni(trien)]

Ni(trien) was prepared with the same procedure used for Cu(trien). Ni(trien) complex was obtained as a purple viscous liquid.

Yield = 0.986 g, quantitative. IR (KBr, cm^{-1}): 3441, 3409 (NH stretching); 2938 (CH stretching); 1546 (asymmetric C=O stretching); 1466 (symmetric C=O stretching); 1402 (CN stretching); 1024 (CO stretching).

RPUR foam preparations

RPUR foam preparation was done as follows. The polyol, catalysts (metal complexes or DMCHA), surfactant, and blowing agent (water) were mixed in a 700-mL paper cup. PMDI was added to the mixed polyol, and the mixture was then stirred by a mechanical stirrer at 2000 rpm for 20 s. The total weights of the starting materials for RPUR foams prepared at indices of 100 and 150 were 26.75 and 33.35 g, respectively. The foam was allowed to rise freely, and during the foaming reaction, the cream time (the time when the foam started to rise or the blowing reaction), gel time (the time when the foam mixture started to gel), tack-free time (the time when the polymerization was finished), and rise time (the time when the foam stopped rising) were measured. For physical and mechanical characterization, the starting materials of the RPUR foams were mixed in a paper cup and poured into a 10.0 × 10.0 × 10.0 cm^3 aluminum mold. The foam was allowed to rise freely, and after the foaming reaction was completed, it was kept at room temperature for 48 h before further characterization. The foam formula-

tions at NCO indices of 100 and 150 are shown in Table I. The NCO index is a measure of excess NCO used relative to the theoretical equivalent amount required to react with polyol and blowing agent (water). It is determined with the following equation:

$$NCO\,index = (Actual\ amount\ of\ NCO\ ued/$$
$$Theoretical\ amount\ of\ NCO) \times 100$$

From Table I, parts by weight (pbw) indicates the weight of the components (in grams) per 100 g of polyol. For example, at an NCO index of 100, the weight of polyol, catalyst, surfactant, blowing agent, and PMDI used were 100.0, 1.0, 2.5, 3.0, and 151 g, respectively.

Because the RPUR foams obtained from different catalysts had similar IR spectra, only the IR data of the RPUR foams obtained from the Cu(en)$_2$ catalyst are shown as follows: IR (IR–ATR, cm^{-1}): 3318 (N—H); 2933, 2874 (C—H); 2277 (free NCO); 1709 (C=O); 1595 (Ar—H); 1515 (N—H); 1412 (C—N isocyanurate); 1309 (C—H); 1220, 1077 (C—O urethane); 814, 766 (C—H aromatic ring).

RESULTS AND DISCUSSION

Synthesis and characterization of M(en)$_2$ and M(trien)

The reactions between metal(II) acetates and aliphatic amines gave M(en)$_2$ and M(trien), as shown in Scheme 1. All of the metal complexes were odorless and had good solubility in the polyol/water/surfactant mixture, whereas copper acetate and nickel acetate were not soluble. The solubility of the metal complexes could be visually observed because all of the metal complexes had colors. The IR spectra of Cu(en)$_2$ and Cu(trien) agreed with the data reported in the literature.[22,23] For Ni(en)$_2$ and Ni(trien), their stretching peaks were different from those of Ni(OAc)$_2$, which
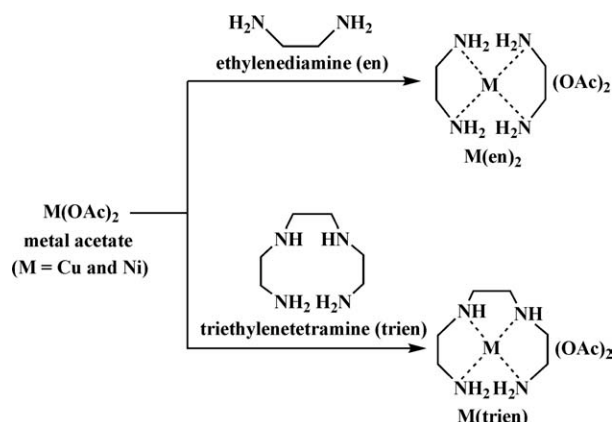
Scheme 1 Synthesis of M(en)$_2$ and M(trien).

TABLE II
Reaction Times and Physical and Mechanical Properties of the RPUR Foams

| | Catalysts at different NCO indices | | | | | | | | | |
| | DMCHA | | Cu(en)$_2$ | | Cu(trien) | | Ni(en)$_2$ | | Ni(trien) | |
	100	150	100	150	100	150	100	150	100	150
Cream time (min:sec)	0:30	0:35	0:35	0:40	0:38	0:44	0:35	0:34	0:36	0:36
Gel time (min:sec)	0:35	0:39	0:41	0:57	0:51	0:59	0:55	1:00	1:23	1:72
Tack-free time (min:sec)	3:00	3:26	1:49	2:36	2:23	3:22	7:35	9:35	11:10	13:30
Rise time (min:sec)	2:40	3:08	2:17	2:57	2:47	3:34	4:49	6:52	7:39	9:06
Density (kg/m^3)	39.6	50.3	40.2	49.8	39.4	48.8	47.7	71.8	46.7	63.9
Compressive strength (kPa)	198.2	321.5	257.0	370.6	237.7	338.5	—	—	—	—

appeared at 1535 cm^{-1} (asymmetric C=O stretching) and 1417 cm^{-1} (symmetric C=O stretching). The absorptions of Cu(en)$_2$ and Cu(trien) in the UV–vis spectra shifted from that of Cu(OAc)$_2$, which appeared at 243 nm. For Ni(en)$_2$ and Ni(trien), weak UV absorption was observed.

Preparation of RPUR foams catalyzed by metal complexes

The polymerization reaction between PMDI, polyol, and water, catalyzed by M(en)$_2$ and M(trien), where M = Cu or Ni, to obtain RPUR foam was studied (Table I). The reaction times for polymerization investigated in this study were the cream time, gel time, tack-free time, and rise time (Tables II and III). The data reported in Tables II and III are average values. The experiments were repeated to obtain standard deviation of less than 10% from the average values. For all metal complexes and DMCHA, the standard deviations of their cream time and gel time were in the range 0.01–0.03. For tack-free time and rise time, the standard deviations in the case of Cu(en)$_2$, Cu(trien), and DMCHA were in the range 0.05–0.10 min. Because Ni(en)$_2$ and Ni(trien) gave longer reaction times, the standard deviations of their tack-free time and rise time were in the range 0.05–0.15. It was found that Cu(en)$_2$ and Cu(trien) showed comparable catalytic activity to DMCHA. For Ni(en)$_2$ and Ni(trien), it was found that the tack-free time obtained from both nickel complexes was longer than that of DMCHA. RPUR foams prepared by Ni(en)$_2$ and Ni(trien) were brittle materials; this indicated that the nickel complexes were not good catalysts. Therefore, further study was done on the polymerization reaction catalyzed by Cu(en)$_2$ and Cu(trien).

NCO conversion was determined from the absorption band of the NCO group at 2277 cm^{-1} in the ATR–IR spectra, as shown in the following equation:[24]

$$\text{Isocynate conversion}(\%) = [1 - (\text{NCO}^t/\text{NCO}^i) \times 100]$$

where NCO^t is the area of isocyanate peak at time t, which is the time after the foam was kept at room temperature for 48 h to complete the polymerization reaction, and NCO^i is the area of isocyanate peak at the initial time. The NCO peak area was normalized by the aromatic ring peak area at 1595 cm^{-1}. It was found that NCO conversion slightly decreased with increasing content of NCO indices. The NCO conversions of RPUR foams catalyzed by Cu(en)$_2$, Cu(trien), and DMCHA at an NCO index of 100 were 98.9, 99.6, and 99.5, respectively, whereas those at an NCO index of 150 were 98.1, 98.8, and 98.9, respectively. It was observed that RPUR foams could be prepared with high NCO conversion at indices of 100 and 150. When RPUR foam was prepared with Cu(en)$_2$ at an NCO index of 200, the polymerization reaction was not completed because a large NCO peak could be observed.

The polymerization reactions using copper complexes exhibited similar rise profiles to that of DMCHA, in which the time to initiate the reaction was short and a fast rise curve in the latter stage was observed (Fig. 1). In comparison to DMCHA, the use of Cu(en)$_2$ and Cu(trien) changed the rise profile of the RPUR foams. This might have been due to the different activity of each catalyst in the reaction between NCO and water to give CO$_2$ (blowing reaction).

TABLE III
Effect of Different Amounts of Catalysts on the Reaction Times and Densities of the RPUR Foams Prepared at an NCO Index of 150
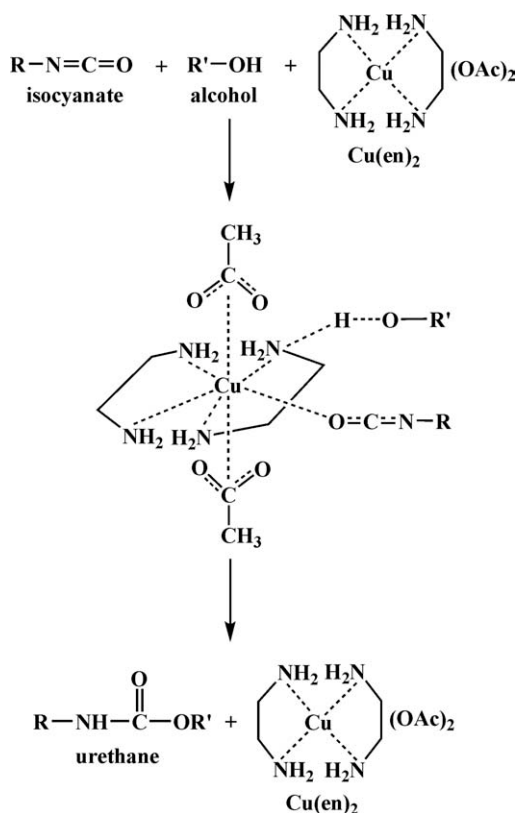
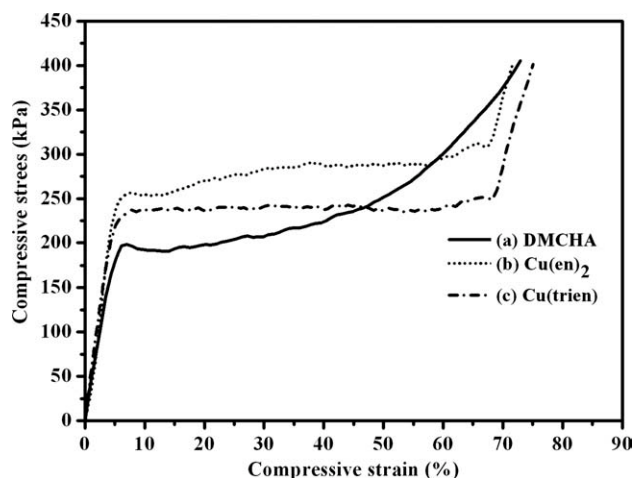| | Catalyst amount (pbw) | | |
Catalyst	0.5	1.0	2.0
Cu(en)$_2$			
Cream time (min:sec)	0:44	0:40	0:34
Gel time (min:sec)	1:22	0:57	0:40
Tack-free time (min:sec)	5:44	2:36	1:30
Density (kg/m^3)	54.4	49.8	45.9
Cu(trien)			
Cream time (min:sec)	0:46	0:44	0:42
Gel time (min:sec)	1:31	0:59	0:51
Tack-free time (min:sec)	5:27	3:22	1:49
Density (kg/m^3)	51.9	48.8	45.4
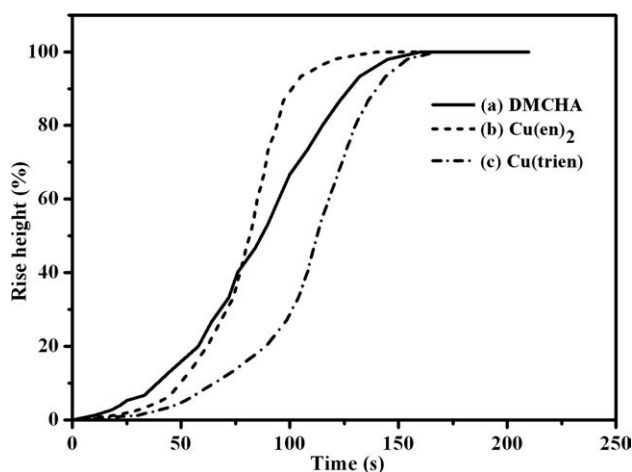
Figure 1 Rise profile of RPUR foams catalyzed by (a) DMCHA, (b) Cu(en)$_2$, and (c) Cu(trien) at an NCO index of 100.

Figure 2 Parallel compression stress–strain curve of RPUR foams catalyzed by different catalysts at an NCO index of 100.

Proposed mechanism of the reaction catalyzed by copper complexes

From Table III, it was found that there was a large decrease in gel time and tack-free time with increasing content of catalyst in the foam formulation. For cream time, only a small decrease was observed. This suggested that the copper complexes were good catalysts for the reaction between NCO and hydroxyl groups to give urethane linkage (gelling

Scheme 2 Proposed catalytic mechanism of Cu(en)$_2$.

reaction). The foam density decreased with increasing amount of Cu(en)$_2$ and Cu(trien). Although a high catalyst quantity at 2.0 pbw gave faster reaction times, the gel time and tack-free time were too short and, therefore, caused difficulty in foam preparation. From the previous data, the reaction scheme for the urethane formation catalyzed by Cu(en)$_2$ is proposed (Scheme 2). Cu(en)$_2$ could catalyze the reaction because the copper atom could act as a Lewis acid and coordinate to the oxygen atom of the NCO group; this caused the NCO carbon to be more electrophilic. The nitrogen atom in Cu(en)$_2$ interacted with the proton of the hydroxyl group and caused the hydroxyl oxygen to be more nucleophilic; this oxygen then reacted with the NCO group to give a urethane linkage. The catalytic mechanism of Cu(trien) was similar to that of Cu(en)$_2$. The reaction times in RPUR foam preparation with Cu(trien) were slower than those of Cu(en)$_2$ because of the steric hindrance of the trien group.

Physical and mechanical properties of the RPUR foams

The free-rise density of the RPUR foams (Table II) catalyzed by copper complexes was close to those prepared from DMCHA. When the NCO index was increased, the density of the foams also increased because the excess NCO could undergo further polymerization to give allophanate, biuret, and isocyanurate structures. Nickel complexes gave brittle RPUR foams with high densities. The compression stress–strain curves of the RPUR foams catalyzed by copper complexes (Fig. 2) showed three stages of deformation, namely, initial linear behavior, a linear plateau region, and densification. The RPUR foams catalyzed by Cu(en)$_2$ and Cu(trien) exhibited higher compressive strength than those prepared from
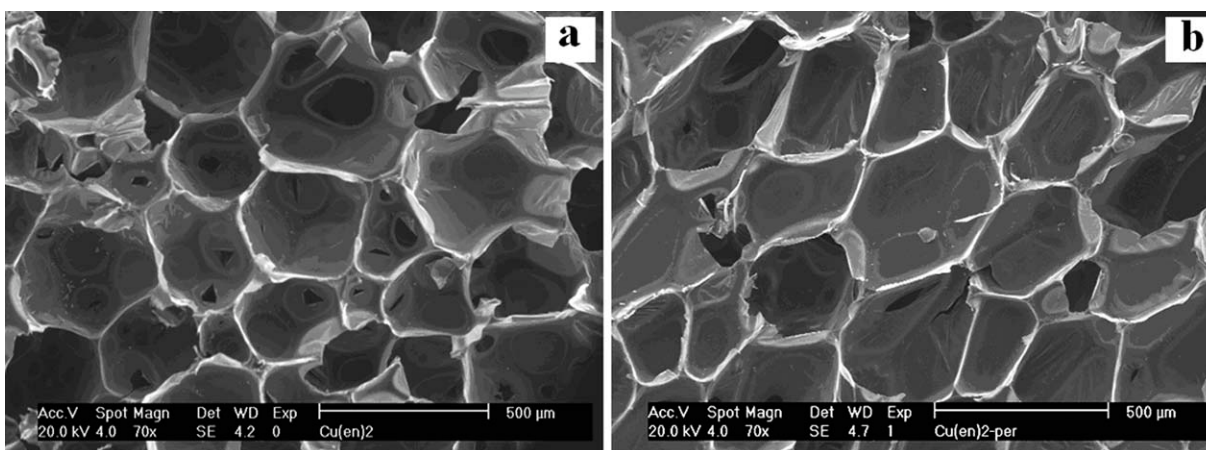
Figure 3 Scanning electron micrographs of RPUR foams catalyzed by Cu(en)$_2$ at an NCO index of 100 (a) parallel and (b) perpendicular to the foam-rising direction (70×).

DMCHA at both NCO indices of 100 and 150. In a comparison between the RPUR foams prepared from Cu(en)$_2$ and Cu(trien), Cu(en)$_2$ gave RPUR foams with higher compressive strengths. The foams prepared at an NCO index of 150 had higher compressive strengths than those prepared at an NCO index of 100. This could have been due to the formation of allophanate, biuret, and isocyanurate structures from the reaction of excess NCO at the NCO index of 150. These reactions caused the RPUR foams to have more crosslinking structures, and therefore, the foams showed a higher compressive strength. The morphology of the RPUR foam catalyzed by Cu(en)$_2$ (Fig. 3) showed that the foam had a closed cell structure. The cell morphology was spherical and elongated in shape in the parallel and perpendicular directions, respectively, of foam rising.

The TGA and derivative thermogravimetry (DTG) thermograms of the RPUR foams catalyzed by Cu(en)$_2$, Cu(trien), and DMCHA [Fig. 4(A,B)] showed the decomposition of the foams in one step. The foams prepared from copper complexes showed similar thermal stability to that prepared from DMCHA. The initial decomposition temperature, which was the temperature at 5% weight loss, was in the range 272–285°C. The residual weight at 600°C was in the range 40–42%. The maximum decomposition temperature was in the range 332–337°C.

CONCLUSIONS

M(en)$_2$ and M(trien) were synthesized with a simple procedure. Cu(en)$_2$ and Cu(trien) showed catalytic activities comparable to that of DMCHA, whereas the nickel complexes were not good catalysts. IR spectroscopy indicated that the polymerization catalyzed by Cu(en)$_2$ and Cu(trien) resulted in quantitative NCO conversion. The RPUR foams prepared

from copper complexes had densities in the range around 40–50 kg/m^3, which was close to those prepared from DMCHA. The compressive strengths of
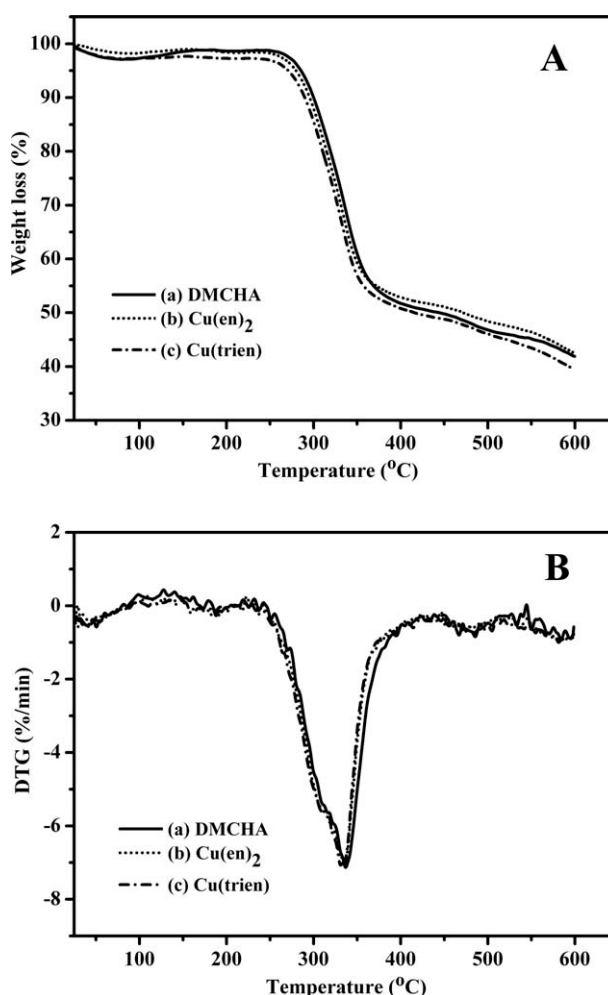
Figure 4 (A) TGA and (B) DTG thermograms of RPUR foams catalyzed by (a) DMCHA, (b) Cu(en)$_2$, and (c) Cu(trien) at a NCO index of 150.

the RPUR foams prepared from Cu(en)$_2$ and Cu(trien) were higher than that of those prepared from DMCHA.

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