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$NdCl_3$-Schiff Base Complex as Catalyst for Formation of Water-Blown Semi-Rigid Polyurethane Foam

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Neodymium chloride Schiff base complex was synthesized and characterized by scanning electron microscopy, elemental analysis, ^1H NMR, FT-IR and complexometric titration. This complex, combined with triethylenediamine, was used as a catalytic composite for the foaming reaction of all-water blown semi-rigid polyurethane foam. The effect of ratio of the complex to triethylenediamine on the properties of reaction product was investigated. This catalytic composite can be in place of organic tin catalyst such as stannous octoate, dibutyl tin dilaurate and other conventional polyurethane foam catalyst, which are usually unstable and toxic, leading to environmental hazards.

Keywords: Schiff base complexes of neodymium chloride, Catalyst, Water foaming, Polyurethane foam.

INTRODUCTION

In recent years, great progress has been made in the field of polymer with rare earth metals as catalyst[1-6]. It is shown that rare earth catalysts possess excellent catalytic performance for the formation of polymers[7]. Novel rare earth catalysts have attracted more and more attention. The complexes of Schiff bases and rare earth metal are widely used as catalysts in scientific research and industrial production[8]. Polyurethane (PU) foam is always synthesized by the reaction of a polyether/polyester-polyol and a polyisocyanatein with the presence of catalyst and a series of additives. Polyurethane foam has a special structure with alternate soft segments and hard segments in the molecular chain. The aggregation structures from micro-phase separation give unique properties for polyurethane foam. Because of its large-scale production and mature manufacturing processes, semi-rigid polyurethane foam is widely used in construction, automotive, decoration and other fields[9-12]. There are many reports about semi-rigid polyurethane water blown foam[13]. But study on the Schiff base complexes of rare earth as catalysts for water blown semi-rigid polyurethane foam is still very limited. This work investigated the use of neodymium chloride Schiff base complexes mixed with ethylene diamine compound as a catalyst for the preparation of water blown semi-rigid polyurethane foam and explored the effect of different proportions of complex to ethylene diamine on the performance of semi-rigid polyurethane foam. The one-step method is employed for the preparation.

EXPERIMENTAL

Polyether polyols MA–4110 (Changzhou Mid-Asia Chemical Co., Ltd., China); diphenylmethyl propane diisocyanate PM-200 (MDI, Wanhua Chemical Group Co., Ltd., China); Silicone oil SD-201 (Siltech New Materials Co., Ltd., China). Triethylene diamine and stannous octoate [$Sn(Oct)_2$] (Sinopharm Chemical Reagent Co., Ltd., China) was purified according to the method described in literature. *Tris*(2-hydroxyethyl)amine and ethylene glycol (Sinopharm Chemical Reagent Co., Ltd., China) were treated by refluxing with phthalic anhydride. Mold discharging agent and rare earth catalyst were homemade.

FT-IR (MAGNA-1R 550 FTIR, America); ^1H NMR (Varian, VNMRS600, America); FESEM (SUPRA 55 Sapphire, Germany); Foaming mould (homemade).

Preparation and characterization of catalysts: 35 mL of salicylaldehyde and 100 mL ethanol was added to a 500 mL flask. This mixture was stirred for 20 min, followed by the addition of a solution of 10 mL of ethylenediamine and 50 mL of anhydrous ethanol. Then this resultant mixture was heated at 78 °C for 2 h. After cooling to room temperature, the reaction mixture was placed in an ice bath and the yellow precipitate was collected by filtration and washed with anhydrous ethanol, then the product was further purified by recystallization with ethanol and vacuum dried 2 h, as a result the yellow crystals of Schiff-base ligand can be obtained.

Anhydrous neodymium chloride (3.302 g), Schiff-base ligand (7.12 g) and 40 mL anhydrous ethanol were added to a flask. This mixture was heated, with stirring, at 80 °C for 3 h and then cooled to room temperature. The precipitate was collected by filtration and washed with anhydrous ethanol to give product which was used as catalyst.

Preparation of combination material and foaming process

Component A: The polyether polyol, catalyst, cross-linking agent and foaming agent were mixed according to an appropriate proportion given in Table-1 and stirred at room temperature.

Component B: MDI: The component A was added to a beaker with stirring, followed by the addition of component B over 10 sec. This reaction mixture then was poured into a mould which maintained at constant 50 °C. Foaming mold was released after 4-6 min and the whole water foaming polyurethane foam was obtained.

TABLE-1
MASS RATIOS OF COMPONENT IN ONE STEP PREPARATION

Component	Proportion
Polyether polyols MA-4110	100 pbw
Triethylene-diamine	2 pbw
Silicone oil	0.5 pbw
$NdCl_3$ Schiff base complexes catalyst	0.1 pbw
Ethylene glycol	1 pbw
Distilled water	1 pbw
Triethanolamine	1 pbw
MDI PM-20	100 pbw

The whole water foaming polyurethane foam was cured at room temperature for 72 h and then its bubble pore structure, density, compressive strength and other performance indexes were measured.

Determination of apparent density of foam: The foam was shaped according to the Chinese national standards (GB/T6343-2009) to measure the mass and volume and calculate the apparent density of foam compression performance. The test was carried out following Chinese national standards (GB/T 8813-2008).

Measurement of dimensional changes after Laundering: The sample foam was kept in refrigerator and dryer at -3 and 53 °C for a month respectively, the dimensional changes was measured by field emission scanning electron microscope (FESEM).

RESULTS AND DISCUSSION

Schiff base: The Schiff base was recrystallized then vacuum dried to constant weight, with yield of 93.1 %. Schiff base ligand was analyzed using ^{1}H NMR shown in Fig. 1. ^{1}H NMR($CDCl_3$) data are as follows. δ: 13.19 (s, 2H, OH), 8.36 (d, 2H, CH=N), 6.83-7.29 (m, 10H, C_6H_5-), 3.93 (t, 4H, N-CH_2-CH_2-N).

Infra spectroscopy of this Schiff base ligand was measured by FT-IR (KBr background), as shown in Fig. 2. FT-IR data: ν = 1635 cm^{-1}, C=N.

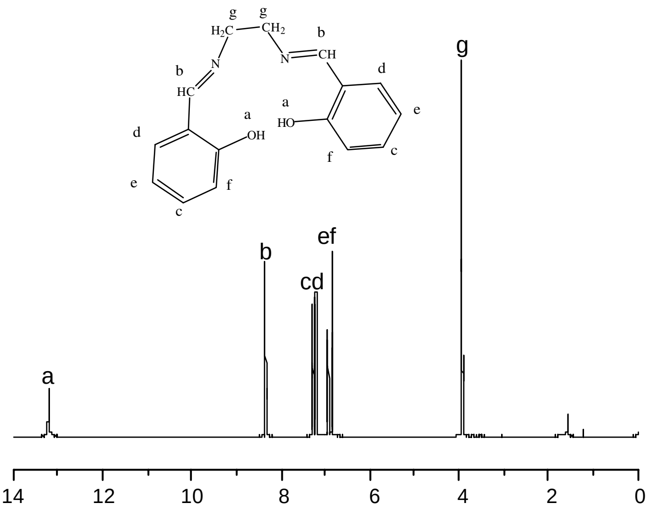

Fig. 1. ^{1}H NMR spectrum of Schiff base

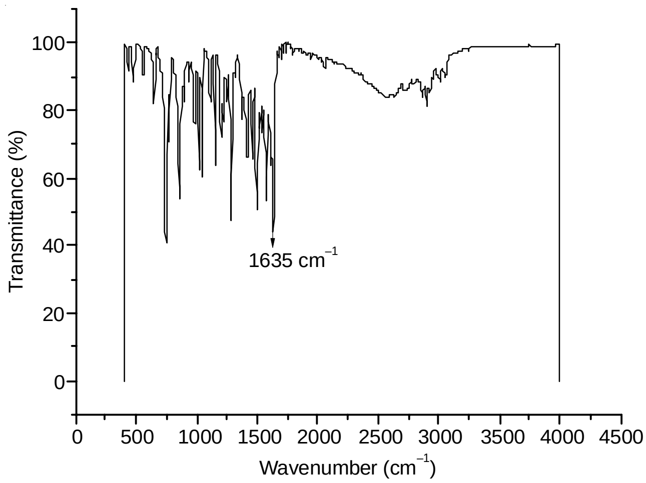

Fig. 2. FT-IR spectrum of Schiff base

$NdCl_3$ Schiff base complexes (catalyst): The catalyst which was obtained by the reaction of neodymium chloride with Schiff base ligand was vacuum dried after washing by anhydrous ethanol, with yield of 86.3 %. Rare earth metal element content was measured by complexometric titration and neodymium content is shown at 16.9 % which is close to the calculated value of 16.7 %. Halogen element content is determined by silver nitrate precipitation, which shows that the chloride ion content is 11.8% closed to the calculated value of 12.1%. In infrared spectra, the C=N absorption moves from 1647 cm^{-1} (Schiff base ligand) to 1635 cm^{-1} after the formation of neodymium chloride Schiff base complexes (Fig. 3).

The complex was characterized by ^{1}H NMR. The spectrum was shown in Fig. 4 and the data are as following: δ: 13.37 (s, 2H, Ar-OH), 8.26 (s, 2H, CH=N), 7.30, 6.89 (m, 10H, C_6H_5-), 3.84 (m, 4H, N-CH_2-CH_2-N), 4.39 (t, 1H, CH_3CH_2OH), 3.43 (m, 2H, CH_3CH_2OH), 1.06 (t, 3H, CH_3CH_2OH). The complex formula was deduced to be $Nd(H_2Salen)_2Cl_3 \cdot 2C_2H_5OH$.

Effect of catalyst on the evaluation results of whole water foaming semi-rigid polyurethane foam: The comparison of semi-rigid foam prepared by the catalyst of $NdCl_3$ Schiff base complexes and prepared using stannous octoate was shown in Table-2. The whole water foaming semi-rigid

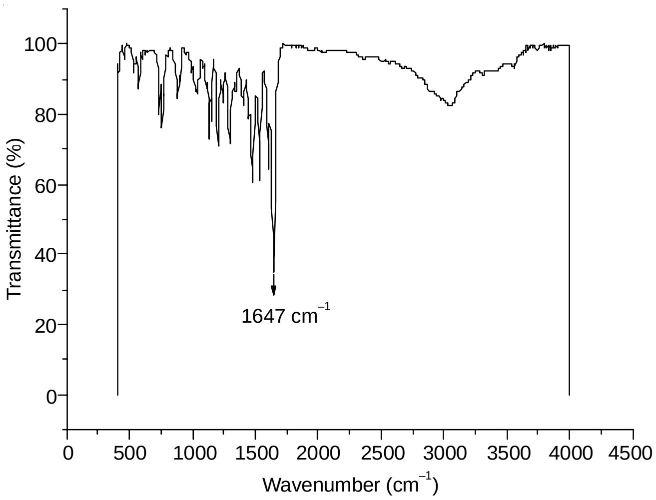

Fig. 3. FT-IR spectrum of NdCl$_3$ Schiff base complexes catalyst

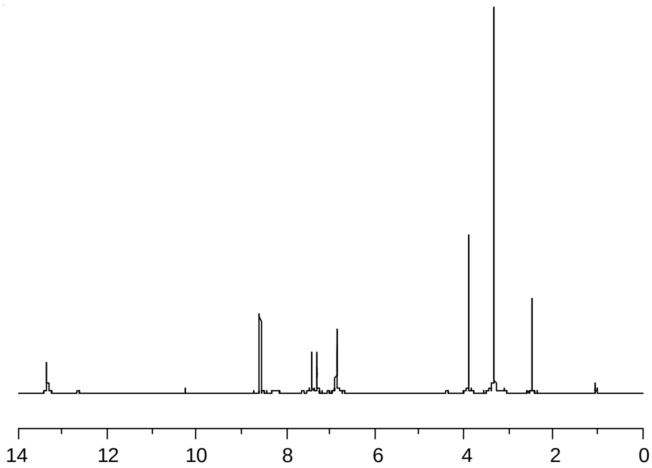

Fig. 4. ^{1}H NMR spectrum of NdCl$_3$ Schiff base complex catalyst

polyurethane foam was obtained by using the composite catalyst, NdCl$_3$ Schiff base complexes and triethylene diamine, stannous octoate and triethylene diamine, respectively.

Based on Table-2, with the increase of rare earth catalyst, the whiteness, gelation and demoulding time increase as well as the reaction rate is easy to control. In the process of foaming, the chain growth and the foaming reaction reach a steady balance. The foaming process will produce a large amount of CO_2 and the addition of rare earth catalyst promotes the balance between foaming process and CO_2 producing rate. Strong bubble wall therefore will form while foaming, which assists to hold the produced gas and lead to the more uniform foaming. The foam has better solidification and the bubble is not easy to collapse and shrink, as result the foam has good formability and stable density. Due to the unstable and oxidation properties of Sn(Oct)$_2$ catalyst and heat producing in foaming process, the catalytic capability of stannous octylate is decreased, leading to poor foaming process stability. Bubbles formed are prone to collapse and shrinkage. Therefore the foam product with rare earth catalyst has better quality because of more uniform and stable bubble pore structure.

Influence of catalyst on mechanics properties of whole water foaming semi-rigid polyurethane foam: The mechanical property of polyurethane foam is mainly decided by the nature of the polymer, volume ratio of gases in the products and bubble size and other geometric properties[14]. The catalyst will decide the rate and content of gas produced to some extent in the foaming process; thus affects the bubble pore shape and pore size distribution directly. The experimental results shown in Fig. 5 indicate that different mass ratio of rare earth catalyst to triethylene diamine will influence mechanical properties of the foam products.

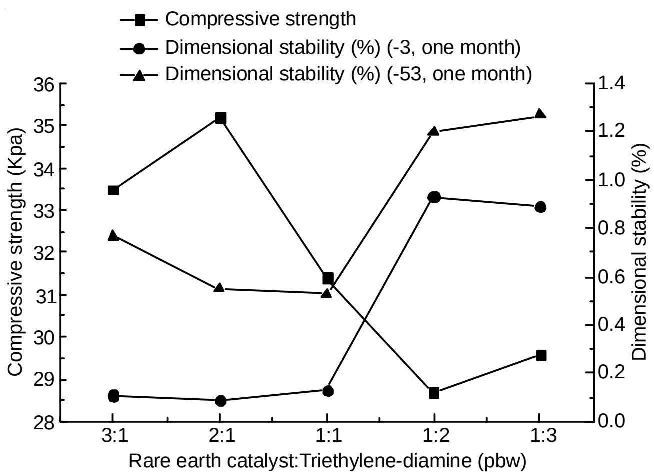

Fig. 5. Effect of catalyst on mechanical properties of foam products

Based on Fig. 5, with the increase of rare earth catalyst, compression strength tends to decrease after the initial increase. But the dimensional changes in different temperature show increase after the initial decrease. In general, the performance of the products is gradually improved and has better dimensional stability, due to using the rare earth catalysts and triethylene diamine in the foaming process. The rare earth can interact with the carbonyl group in the polyurethane system, which affects the hydrogen bonding structure of polyurethane system and lead to structure change in polyurethane foam[15,16]. Therefore with the increase of the proportion of rare earth catalysts in the catalytic system, the compression strength and dimensional stability of the polyurethane foam increase.

TABLE-2
REACTION PROFILES OF WHOLE WATER FOAMING SEMI-RIGID POLYURETHANE FOAM IN DIFFERENT RATIOS OF CATALYST

Catalyst (pbw)	A:B = 1:1	A:B = 1:2	A:B = 2:1	C:B = 1:1	C:B = 1:2	C:B = 2:1
Cream time (s)	15	13	19	7	9	8
Gelation time (s)	48	40	59	35	38	43
Stripping time (s)	278	270	285	353	360	366
Foam density (kg/m^3)	70.6	73.8	76.4	70.9	72.8	70.5
Compatibility	Common	Preferably	Good	Common	Common	Errand

A: Rare earth catalyst, B: Triethylene-diamine, C: (Sn(Oct)$_2$

Influence of rare earth catalyst on bubble pore structure of all water foaming semi-rigid polyurethane foam: The influence of catalysts on foam bubble pore structure is shown in Fig. 6. The whole water foaming semi-rigid polyurethane foam was prepared with a catalytic system of neodymium chloride Schiff base complexes and triethylene diamine with quality ratio of 2:1 and with the other one of stannous caprylate and triethylene diamine on the base of the quality ratio of 1:1 respectively.

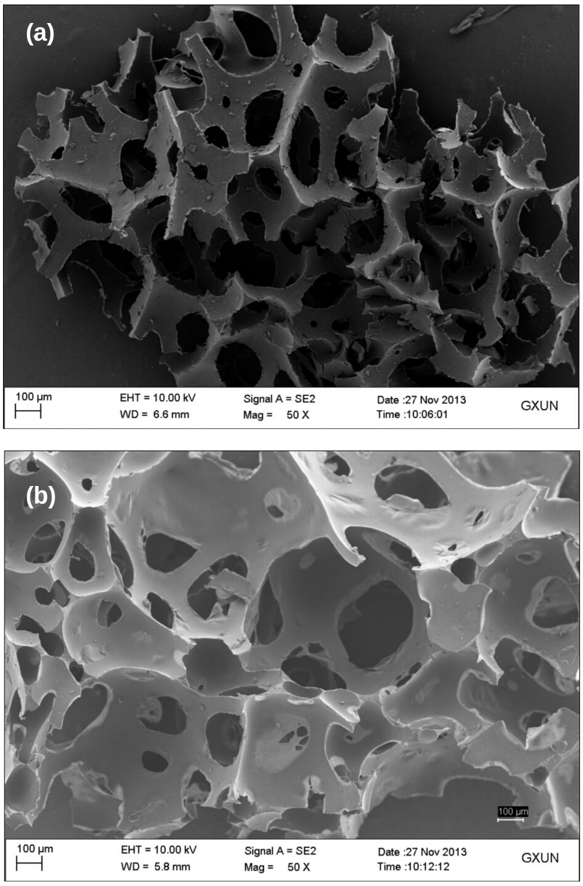

Fig. 6. Bubble figures with different catalyst systems measured by FESEM; (**a**) The pore structure of foam under the catalysis of $NdCl_3$ Schiff Base complex and triethylene diamine catalys; (**b**) The pore structure of foam under the catalysis of stannous caprylate and triethylene diamine

Based on FESEM figures, the foam bubble pore structure is more beautiful and has uniform bubble size with rare earth catalyst. Less fracture section shown compared with that using stannous caprylate catalytic system. Together with the data of Table-2, it is obvious that the foam with good formability and more stable structure was obtained under the catalysis of Schiff base complexes neodymium chloride. Rare earth catalyst in the foaming process promotes the producing rate of gas and gel, resulting in good balance between these two process rates. Due to the unstable properties of stannous in foaming process, the reaction has lower rate of gel and molecular chain growth. As result it lead to the uneven of gas formation rate, the fracture of bubble surface and the non-uniform of aperture size in reaction process.

Conclusion

All water blown polyurethane semi-rigid foam was prepared with neodymium chloride Schiff base complexes and ethylene diamine as catalyst. The compression strength, cell structure and other properties of foam were measured. It is found that, with the ratio of 2:1 of neodymium chloride Schiff base complexes to triethylene-diamine, the foam product shows the best formability, compression strength, dimensional stability at different temperatures and cell structure. With its high catalytic capability, catalyst composed of Schiff base complexes of neodymium chloride and ethylene diamine will make good contribution for the production of polyurethane foam with excellent performance.

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