



Synthesis and fire properties of rigid polyurethane foams made from a polyol derived from melamine and cardanol



Meng Zhang ^{a, b}, Jinwen Zhang ^{c, *}, Shuigen Chen ^a, Yonghong Zhou ^{a, b, **}

^a Institute of Chemical Industry of Forestry Products, CAF, National Engineering Lab for Biomass Chemical Utilization, Key Lab of Forest Chemical Engineering, SFA, Key Lab of Biomass Energy and Material, Nanjing 210042, People's Republic of China

^b Research Institute for Forestry New Technology, CAF, Beijing 100091, People's Republic of China

^c School of Mechanical and Materials Engineering, Materials Science and Engineering Program, Composite Materials and Engineering Center, Washington State University, Pullman, WA 99164, USA

ARTICLE INFO

Article history:

Received 28 May 2014

Received in revised form

23 July 2014

Accepted 11 August 2014

Available online 20 August 2014

Keywords:

Cardanol

Melamine

Polyol

Flame retardant

Polyurethane foams

ABSTRACT

In this work, a melamine and cardanol-derived Mannich base polyol (MCMP) was synthesized via a two-step process. First, cardanol was allowed to react with paraformaldehyde melamine and diethanolamine to yield mixed Mannich bases which were subsequently propoxylated to give the MCMP. Rigid polyurethane foams (RPUFs) were prepared using MCMP and a polyisocyanate. Effects of expandable graphite (EG), ammonium polyphosphate (APP) and diethyl ethylphosphate (DEEP) on the flame retardancy, mechanical properties, thermal stability and morphology of the resultant RPUFs were studied. It was demonstrated that the melamine incorporated into the MCMP molecular structure increased the thermal stability and the flame retardancy of the RPUF. The fire resistance of the foam could be further enhanced by the addition of flame retardants. EG is more effective than APP and DEEP in enhancing the limiting oxygen index of MCMP-based RPUFs. The flame-retardant-filled RPUFs display a better compressive strength, thermal stability, char residue, heat release and smoke emission than does the non-filled foams.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Rigid polyurethane foams (RPUFs) are high volume products and find wide applications in insulation, construction, chemical pipelines, space filling and other applications due to their excellent properties such as closed-cell structure, low thermal conductivity and low moisture permeability [1,2]. However, PUFs are highly flammable and can burn rapidly with a high rate of heat release and notable release of smoke and toxic gases. This high flammability is related to the cellular structure and low density of the foams. Flame retardants (FRs) are often added to the polymer foam products. Current FRs mainly include halogen compounds, phosphorus compounds, metal hydrates and antimony oxide (Sb_2O_3). Halogen-containing FRs (HFRs) are highly effective and still play a major role in many flame retardant plastic products. However, the toxic effects of some HFRs and heavy metal oxides (Sb_2O_3) on human health and environment after disposal have raised serious concerns. Since the

banning of some toxic bromine-containing FRs (e.g brominated diphenyl oxide flame retardants), phosphorus-containing FR (PFRs) have often been proposed as alternatives. In recent years, nitrogen-containing FRs (NFRs) have emerged as a new type of eco-friendly FR alternatives. Their main advantages include low toxicity, limited release of toxic gases and slow evolution of smoke in the event of fire. Melamine and its derivatives are the most important organic nitrogen compounds used as FR additives [3], and they have found applications in different polymer materials [4–8].

PFRs are preferred over HFRs because the former produce less toxic combustion products [9,10]. The flame retardant activity of phosphorus compounds starts in the condensed phase. Upon exposure to heat, phosphorus compounds decompose to produce phosphoric or polyphosphoric acids which catalyze the formation of phosphorus-rich char in the condensed phase [11,12]. Phosphoric acid can react very efficiently with carbodiimide formed by the condensation of the isocyanate released on the thermolysis of PUFs, leading to the formation of carbonaceous char which prevents the heat penetration into the foam surface [13]. In general, nitrogen compounds can interact with phosphorus FRs either synergistically or antagonistically. Various combinations of halogen-free FRs such as ammonium polyphosphate (APP) with melamine, expandable graphite (EG) with triethyl phosphate and red phosphorus, and EG with melamine in the RPUF formulations were recently reported

* Corresponding author.

** Corresponding author. Institute of Chemical Industry of Forestry Products, CAF, National Engineering Lab for Biomass Chemical Utilization, Key Lab of Forest Chemical Engineering, SFA, Key Lab of Biomass Energy and Material, Nanjing 210042, People's Republic of China.

E-mail addresses: jwzhang@wsu.edu (J. Zhang), yhzhou777@sina.com (Y. Zhou).

[14–17]. EG acts mainly in the condensed phase as a smoke suppressant and an insulator. Some studies implied that EG can impart good fire-retardant properties for PUFs [18]. When exposed to a heat source, EG occupies hundreds of times its initial volume and generates a voluminous structure [19]. A “worm-like” structural layer can be formed at the surface of the material due to the expansion of EG during burning. This will prevent heat feedback to the bulk [16], thus providing fire resistance to the polymeric matrix. Alternatively, polyurethanes made from polyols containing a flame-retardant moiety exhibit superior flame-retardant properties and mechanical properties than those containing additive FRs. The application of reactive halogen-free flame-retardant polyols for PUFs has been reported [20–22].

The production of polyurethanes heavily relies on petrochemical feedstock. Nonetheless, synthesis of polyurethanes from renewable resources has been an area of intense research and development for several decades [23–25]. Cashew nutshell liquid (CNSL) is one of a few economically viable sources of naturally occurring phenols. Cardanol is the major ingredient obtained by distillation of CNSL and is considered a very attractive precursor for the production of polyurethanes, phenolic resins, epoxy resins and other bio-based polymers [26–29]. Cardanol has a low viscosity and can be converted to polyols. However, flame-retardant cardanol-derived polyols have not been reported elsewhere.

In this study, a novel flame-retardant polyol with a low viscosity was successfully prepared from cardanol and melamine. Subsequently, RPUFs were prepared using this new polyol, polyisocyanate and/or other FRs with cyclopentane as a blowing agent. In addition to using the flame-retardant polyol for RPUFs, synergistic effects of adding PFRs, ammonium polyphosphate (APP) and diethyl ethylphosphate (DEEP), and commercial unmodified EG to the foams were also investigated. Mechanical properties, thermal stability and fire properties of the new RPUFs were studied in detail.

2. Experimental

2.1. Materials

Cardanol was provided by Shangdong Zibo Trading Company and was a brownish red liquid. The composition of its fatty side

chains varies in degree of saturation, containing ~11.8% saturated hydrocarbons, 65.2% monoolefins and 23.0% diolefins (GC). Reagent grade paraformaldehyde, melamine and diethanolamine (99%) were obtained from Nanjing Chemical Company. Propylene oxide (99.8%) was purchased from Jinling Petrochemical Company. Polyaryl polyisocyanate (PAPI, PM-200) was obtained from Yantai Wanhua Polyurethane Co. (Shandong, China) and contained 30.3 wt% NCO. Expandable graphite (EG) with a medium particle size of 180 μm was obtained from Qingdao Nanshu Hongda Graphite Co. Ammonium polyphosphate (APP) was a product of the Zhenjiang Xingxing Flame Retardant Co. Diethyl ethylphosphate (DEEP) was supplied by Aladdin Chemical Co. The polysiloxane-polyether copolymer (AK8805) was used as a surface active agent and was purchased from Jianguo Maysta Chemical Co.

2.2. Synthesis of melamine modified cardanol-based polyether polyol (MCMP)

2.2.1. Synthesis of cardanol-derived Mannich base

The synthetic route for the cardanol-derived polyol is illustrated in Fig. 1. First, cardanol-derived Mannich base was synthesized in a solvent-free process as follows; 302 g (1.0 mol) of freshly distilled cardanol, 60 g (2.0 mol) of paraformaldehyde and 75.6 g (0.6 mol) of melamine were added to a round-bottomed flask. After the mixture was heated to 60 °C under mechanical stirring, 147 g (1.4 mol) diethanolamine was added drop by drop over approximately 1–1.5 h. Next, the temperature was raised to 90 °C and the mixture was stirred for 2–3 h. Subsequently, the water formed was removed by distillation at reduced pressure and 90 °C to provide a clear brown liquid product.

2.2.2. Synthesis of MCMP

Propoxylation of the above Mannich base product (570 g) with propylene oxide (5.0 mol) was performed at 100–110 °C and a pressure of 0.2–0.3 MPa over a period of 3–4 h. This reaction was catalyzed by the tertiary nitrogen in the structure of Mannich bases (self-catalysis). After the unreacted propylene oxide was removed by distillation at reduced pressure, a viscous yellowish liquid was obtained. The resulting MCMP had a hydroxyl value of 410 KOH mg/g, viscosity of 28.5 Pa s (25 °C) and a moisture content of 0.10%. It

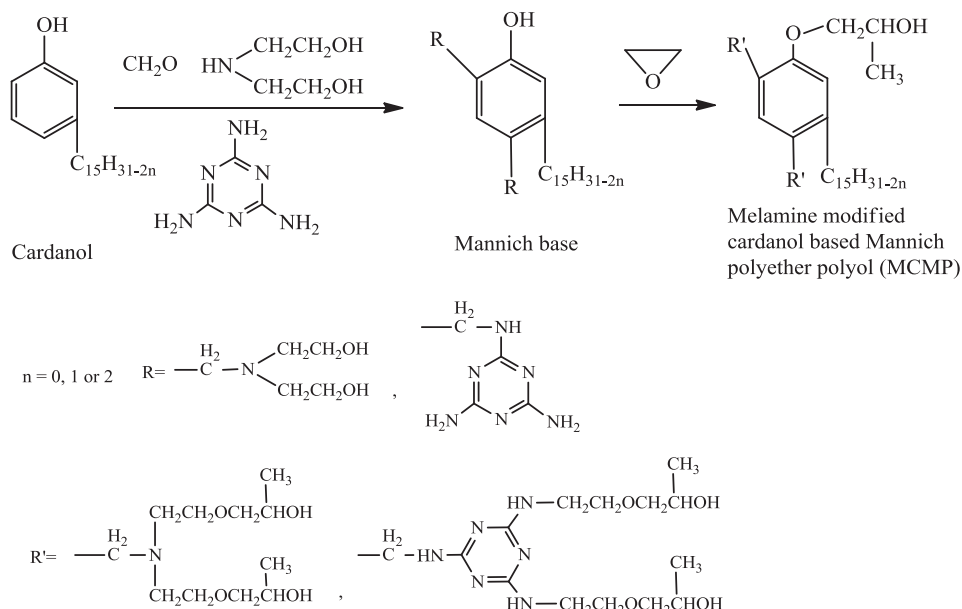


Fig. 1. Synthesis of MCMP.

Download English Version:

<https://daneshyari.com/en/article/5201632>

Download Persian Version:

<https://daneshyari.com/article/5201632>

[Daneshyari.com](https://daneshyari.com)