Industrial Crops and Products 59 (2014) 135–143

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Study of the mechanical, thermal properties and flame retardancy of rigid polyurethane foams prepared from modified castor-oil-based polyols

Meng Zhang[a,*], Hui Pan[b], Liqiang Zhang[a], Lihong Hu[a], Yonghong Zhou[a,*]

[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, PR China
[b] Institute of Chemical Engineering, Nanjing Forestry University, Nanjing, Jiangsu 210037, PR China

ARTICLE INFO

Article history:
Received 14 December 2013
Received in revised form 5 May 2014
Accepted 10 May 2014

Keywords:
Castor-oil-based polyols
Thermal properties
Flame retardant
Polyurethane foams

ABSTRACT

Po1lyurethane foams (PUFs) were prepared using modified castor-oil-based polyols (MCOs). In the first stage, castor oil (CO) was converted into monoglycerides and diglycerides by alcoholysis with glycerol and pentaerythritol. Next, the polyester polyols were synthesised by condensation with the alcoholysis of CO and phthalic anhydride. The chemical and physical properties, foaming behaviour and miscibility with other components of the MCOs were studied by mechanical testing, Fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC) and thermogravimetric analysis (TGA). The results showed that the components of the MCOs and the foaming behaviour of the foams prepared from the MCOs were similar to those of commercial polyester polyol PS-3152. The reaction activities esterification modified CO polyols were higher than those of alcoholysis modified CO polyols, due to the higher relative content of primary hydroxyl groups. The MCOs and CO had higher thermal stability and better miscibility with polyether polyol 4110 and the physical blowing agent cyclopentane than PS-3152. The properties and flame retardancy of PUFs prepared from MCOs were studied by mechanical testing, TGA and cone calorimetry. The results indicate that the PUFs prepared from castor-oil-based polyester polyols with a reasonable distribution of soft and hard segments had better mechanical properties and thermal conductivities than the PS-3152-based PUF5. Additionally, the MCO-modified PUFs exhibited much higher thermal stability during the pyrolysis process. The cone calorimetry results showed that adding flame retardant ammonium polyphosphate (APP) into PUFs can significantly decrease their heat release rate (HRR), total heat release (THR) and mass loss. These test results indicate that APP has a better synergistic effect with phthalic anhydride polyester polyols than long-chain fatty polyols. All of these unique properties of the MCO-modified rigid PUFs were correlated to the structures of these PUFs. This study may lead to the development of a new type of polyurethane foam using castor oil.

1. Introduction

Polyurethane foams (PUFs) are widely used in furniture, packing, insulation and automobile manufacturing. PU materials in the current market are usually made from petro-based polyether or polyester polyol and polyisocyanate through urethane linkages. These petro-based PU products have limited bio-degradability when discarded after use and thus pose an environmental problem (Corcuera et al., 2010; Krämer et al., 2010). Therefore, bio-based materials obtained from renewable resources are receiving considerable attention for use in an increasing number of applications (Campanella et al., 2009; Belgacem and Gandini, 2008; Williams and Hillmyer, 2008) from a social, environmental and energy standpoint due to the increasing emphasis on issues concerning waste disposal and the depletion of non-renewable resources. Vegetable oil is composed of triglycerides of long-chain fatty acids. The most common chain lengths in these fatty acids are 18 or 20 carbon atoms, which can be either saturated or unsaturated at the double bonds located at the 9th, 12th and 15th carbons. They are relatively low-cost materials and offer a priori the possibility of biodegradation. Bio-based materials derived from natural oils, such as castor, palm, canola and soybean oils, have been used to synthesise polyols, which can be used as raw materials in the preparation of bio-based polyurethane foam (Hablot et al., 2008; Petrovic, 2008; Sharna and Kundu, 2008; Xu et al., 2008).

* Corresponding authors. Tel.: +86 25 85482520; fax: +86 25 85413445.
E-mail addresses: zhangmeng82@163.com (M. Zhang), yhzhou777@sina.com (Y. Zhou).

http://dx.doi.org/10.1016/j.indcrop.2014.05.016
0926-6690/

The preparation of various polyurethane products has been extensively studied in recent years, especially those containing biomass-originating raw materials (Hatakeyama and Hatakeyama, 2005; Hatakeyama et al., 2005; Hatakeyema et al., 2005; Kurimoto et al., 2000, 2001). Moreover, it has become clear from previous studies that biomass-based PUs are biodegradable. Castor oil is not edible, does not compete with food and has free secondary hydroxyl groups. Approximately 90% of CO is ricinoleic acid, and the remaining 10% is comprised of oleic and linoleic acids. Ricin oleic acid (C18:1) has an hydroxyl functional group at the 12th carbon, which provides CO with a hydroxyl value of between 160 and 180 mg KOH/g and makes it a favourable raw material for PU products. There are several papers related to the elaboration of PUs based on castor oil, such as interpenetrating polymer networks (Niranjan et al., 2009), elastomers (Oprea, 2010), coatings (Trevino and Trumbo, 2002), adhesives (Somani et al., 2003), and some semi-rigid PU foams that have potential uses in thermal insulation (Ogunniyi et al., 1996; Chian and Gan, 1998; Maznee et al., 2001; Siwayanan et al., 1999) and other interesting applications. Wang et al. (2008) prepared a polyester-polyol (MACO) by chemical modification of hydroxyl groups with maleic anhydride. Then, biodegradable semi-rigid PU foams were synthesised and exhibited mechanical properties comparable to those of a foam derived from commercial polyether. Mazo et al. (2012) studied the kinetics of transesterification and condensation of castor oil with maleic anhydride using conventional and microwave heating.

Although it has been reported that polyurethane obtained directly from CO has good water resistance, desirable mechanical properties and high thermal stability (Ogunniyi, 2006; Yeganeh and Hojati-Talemi, 2007), limitations have also been reported. Due to the low hydroxyl value and the presence of secondary hydroxyls, it has poor reactivity, a slow curing time, low flame retardancy and low miscibility with other components, and it shrinks readily. The modification of CO to increase its hydroxyl value and hard segment composition to improve the rigidity and crosslink density of the final PU products is needed (Baser and Khakhar, 1993; Pan et al., 2008).

The conversion of triglyceride to monoglyceride via glycerolysis is an alternative to epoxidation for the introduction of hydroxyls to CO. By reaction with glycerol or pentaerythritol, two primary hydroxyl groups will be introduced to a monoglyceride molecule derived from CO (Noureddini and Medikonduru, 1997; McNeill and Berger, 1993). The benzene rings could be introduced to the modified castor-oil-based polyol (MCO) as hard segments by esterification with phthalic anhydride. Thus, in the present work, four different polyols were obtained from CO and its immediate derivative from the alcoholysis of CO and reaction with phthalic anhydride. The flame retardant ammonium polyphosphate (APP) was added to the foam to investigate the flame retardancy of PUFs. The properties and flame retardancy of PUFs prepared from MCO were also characterised and compared with traditional PUF based on the polyester polyol PS-3152. The purpose of this study was to synthesise modified castor-oil-based polyols with an appropriate proportion of hard and soft segments and good miscibility with polyether polyols and an environmentally friendly low-VOC foaming agent cyclopentane. In turn, the development of such materials would expand the potential applications of PUFs and polyurethane-based CO, especially in flame retardancy.

2. Experimental

2.1. Materials

Castor oil (hydroxyl value: 163 mg KOH/g) was purchased from Aldrich Chemical Co., Inc. (USA). Polyester polyol (PS-3152) was kindly provided by Stepan Jinling Chemical Co., Ltd. (Nanjing, China). Polyether polyol 4110 (sucrose and diethylene glycol as initiator, hydroxyl value: 403 mg KOH/g, viscosity at 25 °C: 3600 mPa s) was obtained from Jiangsu Qianglin Bio-energy Co., Ltd. PM-200 as the polyaryl polymethylene isocyanate (PAPI) was obtained from Yantai Wanhua Polyurethane Co., Ltd. (Shandong, China). The NCO group content was 30.3% by weight. N,N-dimethyl cyclohexylamine (DMCHA) was used as a catalyst and was kindly supplied by Aladdin Chemical Co., Ltd. Polysiloxane-polyether copolymer (AK8805) was used as the surface-active agent and purchased from Jiangsu Maysta Chemical Co., Ltd. APP was a product of the Zhenjiang Xingxing Flame Retardant Co., Ltd.

2.2. Preparation of castor-oil-based polyols

Approximately 20–40 g of glycerol or pentaerythritol was placed in a 250-ml three-neck round-bottom flask equipped with a water-cooling condenser and a thermometer. Accurately weighed CO was added to the flask in a mole ratio of 1/2. $Ca(OH)_2$ (0.2 g) was then added into the mixture as a catalyst. The alcoholysis reactions were carried at 230 °C for 3 h under an N_2 atmosphere. The alcoholysis reactions with glycerol and pentaerythritol gave products labelled as MCO1 and MCO2, respectively. The alcoholysis products were then modified by phthalic anhydride at a OH/COOH ratio of 3:1 with tetrabutyltitanate as the catalyst. The reaction was maintained at 180 °C for 2 h, increased to 220 °C at a rate of 10 °C/h and then kept at this temperature. The reaction was stopped when the acid value of the reactants was less than 1.5 mg KOH/g. Two MCO-based polyols (MCO3 and MCO4) could be prepared from MCO1 and MCO2, respectively. The reaction schemes of the alcoholysis and condensation are shown in Fig. 1.

2.3. Preparation of castor-oil-based PUFs

Table 1 lists the composition of castor-oil-based rigid PUFs. All materials except for isocyanate were first mixed well in a plastic beaker. Next, isocyanate was added into the beaker and mixed at 3000 rpm for 8 s. To measure the foaming behaviour of the foaming system, approximately 35 g of the total formulation was poured into a 500-ml beaker. The rest of the total formulation was quickly poured into an open mould (200 mm × 200 mm × 300 mm) to produce free-rise foam for the measurement of the physical properties. After the rising was completed, the foams were kept in an oven at 70 °C for 24 h to complete the polymerisation reaction. Different specimen sizes were cut from the cured foam to assess its physical mechanical properties. The final dimensions of the specimens were achieved by rubbing the foams with fine emery papers.

2.4. Characterisations of the MCOs and PUFs

2.4.1. Moisture content, acid value, hydroxyl value and relative content of primary hydroxyl

The moisture content of the MCOs was determined by the Karl Fischer method using a CBS-1A model moisture content meter (Beijing Chao Sheng Co., China).

Table 1
Composition of investigated PUFs.

Samples	PUF1	PUF2	PUF3	PUF4	PUF5	PUF6	PUF7	PUF8
MCO1	100	0	0	0	0	0	0	0
MCO2	0	100	0	0	0	100	0	0
MCO3	0	0	100	0	0	0	0	0
MCO4	0	0	0	100	0	0	100	0
PS-3152	0	0	0	0	100	0	0	100
AK8805	2	2	2	2	2	2	2	2
DMCHA	1	1	1	1	1	1	1	1
Cyclopentane	25	25	25	25	25	25	25	25
APP	0	0	0	0	0	10	10	10
PM-200	110	110	110	110	110	110	110	110