Polymer Testing 70 (2018) 403–412

Contents lists available at ScienceDirect

Polymer Testing

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

Preparation and characterization of boron-containing polyurethane foams with carbazole

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ARTICLE INFO

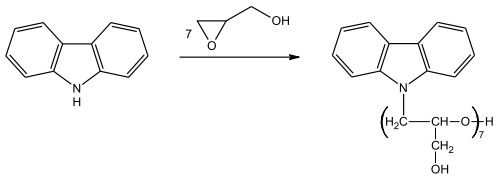
Keywords:
Carbazole
Hydroxyalkylation
Oligoetherols
Polyurethane foams
Properties
Biodegradation

ABSTRACT

Oligoetherol as a reactive retardant was synthesized from carbazole and boric acid in reaction with glycidol and ethylene carbonate. Moreover, melamine, melamine polyphosphate and tris(2-chloro-1-methyl-ethyl) phosphate were used as additive flame retardants. The properties of polyurethane foams obtained from such oligoetherols were investigated. It has been found that melamine is the best flame retardant. The polyurethane foam obtained from oligoetherol synthesized from carbazole, glycidol and ethylene carbonate in 1:7:8 M ratio showed not only high oxygen index (24.7%), but also the highest thermal resistance. This material showed also good mechanical resistance before and after annealing at 175 °C. The experimental results of the bioassays obtained during these investigation show that some of the microorganism have potential to degrade the tested polyurethane foams. This can be seen in data obtained with Colony Forming Unit, where bacteria were able to growth exposed to polyurethane foams, and without any addition of the carbon/energy source.

1. Introduction

Polyurethanes (PU) are one of the most used polymers. The substrates to obtain PU are polyols and diisocyanates. Mechanical properties of such polymers can be tuned by appropriate substrates to get rigid, elastic or semi-rigid polyurethane foams (PUFs). PUFs are used in building construction, clothing, footwear, car, and aviation industries. Their use is limited by thermal instability. Thus the classic PUFs can stand long term heating at 90 °C [1]. Systemic work for improvement of PUF thermal resistance prompted us to incorporate azacyclic 1,3,5-triazine- and perhydro-1,3,5-triazine rings, purine, and carbazole [2–7]. In case of the latter the increase of thermal resistance of PUF was the largest [5]. Synthesis of oligoetherols in carbazole and the use of them to obtain thermally resistant PUFs was described earlier [4]. In the first step the reaction of carbazole (I) with 7-fold molar excess of glycidol led to multifunctional alcohol (II) (see Scheme 1):



(I) (II) (1)

Further reaction with oxiranes (ethylene or propylene oxides; EO and PO) or alkylene carbonates (ethylene or propylene carbonates; EC or PC) resulted in formation of oligoetherols with carbazole ring (III):

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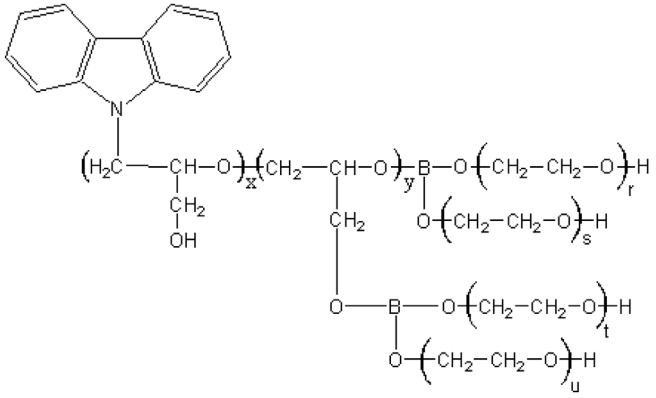
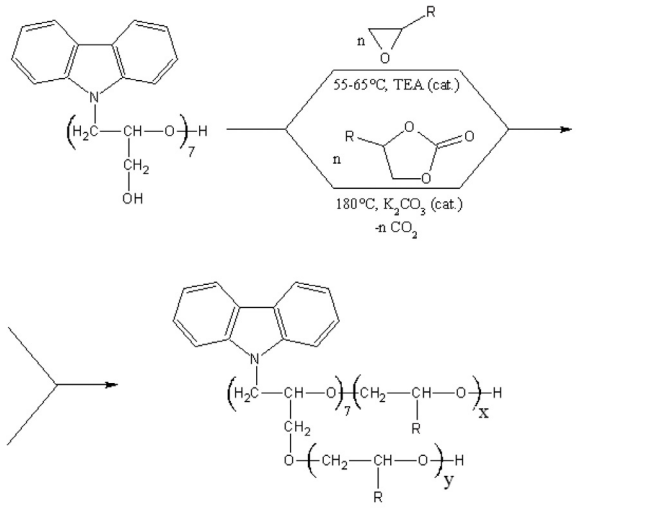
https://doi.org/10.1016/j.polymertesting.2018.07.027
Received 17 June 2018; Received in revised form 20 July 2018; Accepted 28 July 2018
Available online 29 July 2018
0142-9418/



Scheme 1. General structure of polymeric products composed of variable amount of C, G, BA, and EO components. Some of compounds were identified as minor products by MALDI-Toff (see entries in Table 2). Entry 3, Calc. mol. weigh 329.143 g/mol, x = 1, y = 0, s = t = u = 0, r = 1, $–H_2O$ (dehydration). Entry 5, Calc. mol. weigh 359.153 g/mol, x = 1, y = 0, s = r = t = u = 0, $–H_2O$ (dehydration). Entry 8, Calc. mol. weigh 403.180 g/mol, x = 2, y = 0, s = t = u = 0, r = 1, $–H_2O$ (dehydration). Entry 13, Calc. mol. weigh 461.202 g/mol, x = 0, y = 1, u = 0, s = r = t = 1, $-2H_2O$ (dehydration). Entry 21, Calc. mol. weigh 595.479 g/mol, x = 4, y = 0, t = u = 0, r = s = 1 $–H_2O$ (dehydration).



(III) (2)

where R = H lub CH_3

x, y – number of oxyalkylene units derived from oxirane.

x + y = n.

Unfortunately, the obtained PUFs were flammable. The flammability of PUFs can be considerably decreased upon addition of boron, phosphorus, or silicon at the synthesis step (reactive flame retardants) or by addition of non-flammable source of these elements into foaming mixture (additive flame retardants) [8–18].

In this paper we report on attempts to obtain oligoetherols containing carbazole and boron reactive retardant. The source of boron was boric acid. Moreover, melamine (MEL), melamine polyphosphate and tris(2-chloro-1-methyl-ethyl) phosphate were used as additive flame retardants. The PUFs obtained from such oligoetherols were studied for thermal stability and flammability, as well as biodegradation.

2. Experimental section

2.1. Materials

The following materials were used in the work: carbazole (C, pure, Fluka, Switzerland), glycidol (G, pure, Sigma-Aldrich, Germany), boric acid (pure, POCH, Poland), potassium carbonate (pure, POCH, Poland), ethylene carbonate (EC, pure, Fluka, Switzeland), triethylamine (TEA, pure, Fluka, Switzerland), surfactant Silicon L-6900 (pure, Momentive, USA), melamine (M, pure, Merck, Germany), 40–60% melamine poly (phosphate) (MPP, pure Alwernia, Poland), tris(2-chloro-1-methyloethyl) phosphate (TCMEP, pure, European Chemicals Agency, United Kingdom), polymeric diphenylmethane 4,4′–diisocyanate (pMDI, prod. Merck, Germany, content of isocyanate groups 30%).

For PUF biodegradation assay *Pseudomonas aeruginosa* ATCC27853, *Pseudomonas fluorescens* PCM 1994, *Pseudomonas chlororaphis* PCM2210 and *Bacillus subtilis* PCM486 strains (from the bacteria collection of the Faculty of Biotechnology, Rzeszow University, Poland) were employed. Nutrient broth/agar (AO) were purchased from the BTL Company (Poland). For serial dilutions phosphate buffered saline (PBS; NaCl, KCl, Na_2HPO_4, KH_2PO_4 (POCH Gliwice, Poland) and NH_4NO_3 (Chempur, Poland) was used.

2.2. Syntheses

Reaction of carbazole with glycidol at 1:7C:G molar ratio were conducted as described before [4]. The product was isolated as creamy paste.

2.3. Reaction of product of C:G = 1:7 with boric acid and ethylene carbonate

34.3 g (0.05 mol) of C:G = 1:7 reaction product and 6.2 g (0.10 mol) of boric acid (pure, POCH, Poland) were placed in three necked round bottom 250 cm^3 flask equipped with mechanical stirrer, and thermometer. The mixture was heated at 120–130 °C in open flask until desired mass loss related to release of esterification water. Then 0.20 g of potassium carbonate as catalyst and 79.25 g (0.90 mol) EC were added and the mixture was heated at 145–150 °C. The process was continued until consumption of EC.

2.4. Analytical methods

The course of reaction of hydroxyalkylation of EC was followed by measuring the content of unreacted alkylene carbonate. The sample was then treated with 2.5 cm^3 of 0.15 M barium hydroxide, vigorously shaken and the excess of barium hydroxide titrated off with 0.1 M HCl solution [19]. In obtained products the acid numbers were determined by titration with a standard potassium hydroxide solution. Hydroxyl number of the obtained oligoetherols was determined with use of acetic anhydride [20]. Elemental analysis for C, H, N, were done with EA 1108, Carlo-Erba analyzer. The ^1H NMR spectra of products were recorded at 500 MHz Bruker UltraShield in DMSO-d_6 with hexamethyldisiloxane as internal standard. IR spectra were registered on PARAGON 1000 FT IR Perkin Elmer spectrometer in KBr pellets or ATR technique. MALDI ToF (Matrix-Assiated Laser Desorption Ionization Time of Flight) of oligoetherols were obtained on Voyager-Elite Perceptive Biosystems (US) mass spectrometer working at linear mode with delayed ion extraction, equipped with nitrogen laser working at 352 nm. The method of laser desorption from matrix which is of gold. Therefore the observed peaks corresponded to the molecular ions plus Au and K^+ (from catalyst) ions. The samples were diluted with water to 0.5 mg/cm^3.