Industrial Crops and Products 97 (2017) 65–78

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Preparation and modification of water-blown porous biodegradable polyurethane foams with palm oil-based polyester polyol

Wei Seng Ng[a], Choy Sin Lee[b], Cheng Hock Chuah[a], Sit-Foon Cheng[a,*]

[a] Unit of Research on Lipids (URL), Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Department of Pharmaceutical Chemistry, School of Pharmacy, International Medical University, Bukit Jalil, 57000 Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:
Received 11 August 2016
Received in revised form
21 November 2016
Accepted 30 November 2016

Keywords:
Palm oil-based
Polyester polyol
Polyurethane
Water-blown
Biodegradable polymers

ABSTRACT

Water-blown porous polyurethane foams were synthesized by one-shot foaming method. The effect of modification of polyurethane system with different content of newly synthesized palm oil-based polyester polyol (PPP) on the physical, chemical, mechanical and biodegradation properties of polyurethane foams were investigated. The resulting polyurethane foams were characterized by ATR-FTIR, Instron Universal Testing Machine, STA and SEM. The modification of polyurethane with PPP improved pore size and cell compactness, tensile strength, elastic modulus and elongation at break of the polyurethane foams. In terms of biodegradation properties, all the modified polyurethane foams were susceptible to enzymatic degradation. The degradation of modified polyurethane did not incur significant changes in pH of the medium used. After 7 days of enzymatic treatment, polyurethane prepared with 100 wt.% and 75 wt.% of PPP maintained 90% and 70% of the tensile strength, respectively. The current work demonstrated that the modification of water-blown porous polyurethane formulation with PPP allow improvement in physical and mechanical properties as well as tunable degradation rate with sustained mechanical strength, which may suitably use in soft and rigid tissue engineering applications.

1. Introduction

Polyurethane is versatile class of polymer produced by reacting polyester or polyether polyols, with polyisocyanates and chain extenders conventionally (Badri, 2012). However, most polyols used in polyurethane industry are petroleum-based which consume much energy and high technology processing system (Sun et al., 2012; Noor et al., 2013; Badri et al., 2001). Moreover, deepening of oil crisis and environmental issues have promoted the use of renewable resources to replace petrochemical-based polyols due to their feasible route of utilization, inexpensive as well as their environment and sustainability reasons (Hazmi et al., 2013). Numerous researches have outlined the potential of vegetable oil-based polyols derived from soybean oil (Sun et al., 2012), jatropha oil (Hazmi et al., 2013), castor oil (Gao et al., 2012; Luong et al., 2016), cardanol oil (Badri, 2012), rapeseed oil (Zieleniewska et al., 2015) and palm oil (Badri et al., 2001; Tanaka et al., 2008) towards polyurethane applications.

Palm oil, which is produced from oil palm (*Elaeis guineensis*) and commercially cultivated in Malaysia, is one of the most widely used plant oils in the world (Tanaka et al., 2008). Palm oil has been found suitable for many non-food applications in recent years. The present work has the ultimate objective of diversifying the utilization of palm oil and palm oil products as well as value addition to the world's largest oil consumed and produced. Palm oil-based polyols had been prepared by several synthesis pathways, such as epoxidation and ring opening, alcoholysis (Noor et al., 2013), and transesterification (Chuayjuljit et al., 2007) of palm oil. However, there is no reported work on using palm oil-based monoacylglycerols in producing palm oil-based polyester polyol via polycondensation process.

In addition, the reported works on the production of palm oil-based polyols are mainly for rigid polyurethane (Badri et al., 2001; Chuayjuljit et al., 2007). Pawlik and Prociak (2012) reported the influence of palm oil-based polyol on the properties of flexible polyurethane foams. The replacement of petrochemical polyol with palm oil-based polyol up to 15 wt.% resulted in uniformed cell size, increased apparent density, compressive stress and tensile strength of flexible polyurethane foams (Pawlik and Prociak, 2012). However, toluene diisocyanate (TDI) was used as hard segment for the preparation of polyurethane. The release of toxic and carcinogenic aromatic diamine from aromatic diisocyanate might cause a major concern (Wang et al., 2011).

* Corresponding author.
E-mail address: sfcheng@um.edu.my (S.-F. Cheng).

http://dx.doi.org/10.1016/j.indcrop.2016.11.066
0926-6690/

Recently, the development of biodegradable polyurethane with wide range of physico-chemical, mechanical and biocompatibility properties has been the highlight of polyurethane as biomaterials (Luong et al., 2016; Jiang et al., 2007, 2010; Qu et al., 2016) for tissue engineering (Spagnuolo and Liu, 2012), drug delivery systems (Wang et al., 2011), implantable materials (Sister and Lurechko, 2006) and bone graft substitutes (Gogolewski and Gorna, 2006). Ideal biodegradable polyurethane should possess sufficient biomechanical strength to withstand physiologically relevant force, a degradation rate that matches the rate of tissue growth, and over time the load bearing should be gradually transferred to the newly formed tissue (Ruan et al., 2014). Controllable degradation rate of biodegradable polyurethane, either on long-term degradation applications, such as tissue engineering and long-term drug delivery; or rapid degradation polyurethane to be used in clinical treatment applications such as rapid drug delivery system and magnetic resonance imaging (MRI) contrast agent in biomedical imaging (Chuayjuljit et al., 2007) have been investigated (Wang et al., 2011). The degradation rate of polyurethane is determined by the inter and intramolecular forces, crystallinity, hydrophobicity, molecular weight, composition, and swelling behaviour (Tsai et al., 2015). Most importantly, biodegradable polyurethanes and its degradation products must be non-cytotoxic and cause a minimal immune response *in vivo*, which can be achieved by optimizing their compositions and preparation methods (Jiang et al., 2007, 2010; Asefnejad et al., 2011). Typically, polyurethanes containing ester or ether groups are vulnerable to degradation due to hydrolysis *in vivo* (Asefnejad et al., 2011). Among the families of synthetic polymers, aliphatic polyester polyols such as poly(lactic acid) (PLA) (Mi et al., 2013; Fabbri et al., 2016), poly(glycolic acid) (PGA) (Barnes et al., 2007), poly(lactic-*co*-glycolide) (PLGA) (Park et al., 2005), poly(*ortho*-esters) (POE) (Andriano et al., 1999) and polycaprolactone (PCL) (Gisele et al., 2011; Guan et al., 2007) have been used for this application due to their degradation by hydrolysis of ester bonds to form resorbable degradation products (Wang et al., 2011). However, all these commonly used polyester polyols are derived from petrochemicals.

Besides the polyol components, isocyanate with the reactive N=C=O functional group is also an important component forming the hard segment of polyurethane. Most of the polyurethane products, including polyurethane for biomedical applications are still mainly produced from aromatic isocyanates, namely, toluene diisocyanate (TDI) (Dong et al., 2009), methylene diphenyl diisocyanate (MDI) (Gonzalez-Paz et al., 2013) and polymeric methylene diphenyl diisocyanate (pMDI) (Hridya and Jayabalan, 2009). For instance, commercial medical-grade polyurethanes prepared from MDI are Biomer®, Elasthane™ and ChronoFlex® AR (Reed et al., 1994). Concerns on the release of carcinogenic and mutagenic aromatic diamines compounds from aromatic diisocyanate-based polyurethane during biodegradation have been raised (Guelcher et al., 2005). Lately, aliphatic diisocyanates such as hexamethylene diisocyanate (HMDI) (Ruan et al., 2014; Serkis et al., 2015; Kupra et al., 2016), isophorone diisocyanate (IPDI) (Jiang et al., 2007, 2010), and ethyl lysine diisocyanate (Adhikari et al., 2008) have increasingly been used in biomedical applications considering its degradation products are more likely to be less toxic than the aromatic-based polyurethane (Jiang et al., 2010; Ruan et al., 2014; Serkis et al., 2015). The preparation of biodegradable polyurethane from aliphatic isocyanates is still relatively scarce because aliphatic isocyanate is comparatively less reactive than of aromatic isocyanate (Eram and Fahmina, 2012). In view of the environmental and sustainable issues, coupled with the potential of polyurethane as biomaterials, the aim of this work is to produce the water-blown porous polyurethane by using the newly synthesized palm oil-based polyester polyol (PPP) with controllable biodegradation properties.

The water-blown porous polyurethanes were produced by substituting petroleum-based commercial polyols, *i.e.* polyethylene glycol (PEG) and polycaprolactone diol (PCL) with the newly synthesized palm oil-based polyester polyol (PPP) by one-shot foaming method. PPP was synthesized by direct polycondensation of deacidified palm oil-based glycerol monostearate (DGMS) with glutaric acid in a non-catalyzed and solvent free condition. The effects of modification of polyurethane system with different content of PPP on the physical, chemical, mechanical, thermal and biodegradability properties of the polyurethane were investigated and comparisons were made with the reference foam produced from a mixture of PEG and PCL. The polyurethane foams were characterized by Attenuated Total Reflection – Fourier Transform Infrared (ATR-FTIR), Instron Universal Testing Machine, Simultaneous Thermal Analyzer (STA) and Scanning Electron Microscope (SEM). The modification of polyurethane with PPP allow improvement in physical and mechanical properties as well as tunable degradation rate with sustained mechanical strength. By blending with different percentages of PPP with commercial polyols, the water-blown porous polyurethane has shown great potential as biomaterial for medical applications such as soft and rigid tissue engineering.

2. Experimental

2.1. Materials

Glycerol monostearate (GMS) was provided by InterMed Esters Sdn. Bhd. GMS was deacidified with cyclohexane prior to use. Glutaric acid (99%), glycerol, dibutyltin dilaurate (DBTDL) and isophorone diisocyanate (IPDI) were purchased from Merck. Polyethylene glycol (PEG, number average molar mass, M_n = 6000 Da) and polycaprolactone diol (PCL, number average molar mass, M_n = 2000 Da) were purchased from Fischer Scientific. Niax catalyst A33 (triethylenediamine, TEDA) and Niax silicone surfactant L580 were purchased from Samchem Holding Berhad. Lipase Type II from porcine pancreas (Lipase activity: 100–400 U/mg protein) was purchased from Sigma-Aldrich. All chemicals were used as received.

2.2. Synthesis of palm oil-based polyester polyol (PPP)

PPP was synthesized via polycondensation of deacidified glycerol monostearate (DGMS) and glutaric acid in the molar ratio of functionality (OH:COOH) of 1:0.6 at 200 °C for 12 h (Fig. 1). DGMS and glutaric acid were placed in a 500 mL three-neck round bottom flask that was equipped with a dean & stark, a cooling condenser, a thermometer and a magnetic stirrer. The reaction mixture was heated in a heating mantle with continuous stirring under vacuum to remove water by-product formed. PPP was withdrawn hourly to optimize the reaction through acid value (AV) and hydroxyl value (OHV) analyses according to American Oil Chemists' Society (AOCS) Official Method Te 2a-64 and AOCS Cd 13–60, respectively.

2.3. Characterization and analyses of palm oil-based polyester polyol (PPP)

The weight average molecular weight (M_w) and polydispersity index (PDI) of the PPP were measured by using Viscotek GPCmax VE 2001 machine. The viscosity of PPP was determined using Rheometer (TA instruments DHR-2) at 45 °C and 60 °C. The DSC thermogram of PPP was obtained using DSC823e (Mettler Toledo) instrument. Approximately 5 mg of sample was weighed and analyzed at heating range from −10 °C to 100 °C with a flow rate of 10 °C/min under