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Sustainable flame-retardant polyurethanes using renewable resources

Sanket Bhoyate[a], M. Ionescu[b], P.K. Kahol[c], Ram K. Gupta[a,b,*]

[a] Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762, USA
[b] Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS 66762, USA
[c] Department of Physics, Pittsburg State University, Pittsburg, KS 66762, USA

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ABSTRACT

Renewable bio resources such as soybean, orange peel, and castor along with a novel phosphorous based polyol were used to prepare highly flame-retardant polyurethane foams. Diethyl allyl phosphonate (DEAP) and thioglycerol (TG) were used to synthesize phosphorous (P) based flame retardant polyol (DEAP-TG). Polyurethane (PU) foams having a various weight percentage of phosphorous were prepared using a varying amount of DEAP-TG (as a phosphorous source) and other bio-based polyols. Use of DEAP-TG polyol in polyurethane foams showed improved compressive strength without affecting closed cell content and morphology of the foams. The horizontal burning test showed a drastic reduction in self-extinguishing time and weight loss for the PU foams containing DEAP-TG polyol. For example, castor oil and DEAP-TG based PU foam which contains 1.5 wt% P showed significant reduction in self-extinguishing time (from 94s to 1.7s) and weight loss (from 48.5% to 3%) compared to neat castor oil based foams. Cone calorimeter data also showed a significant reduction in peak heat release rate, total heat release, total smoke release, and overall smoke production rate for the foam containing 1.5 wt% P compared to 0 wt% P in the foam. The improved flame retardancy was due to the formation of a protective char layer over the surface of the foam due to decomposition of a phosphorus compound. Our research provides a green alternative to prepare industrial grade flame-retardant polyurethane foams.

1. Introduction

Polyurethanes (PUs) using bio-based materials are attracting considerable research and commercial attention due to sustainability issue (Ionescu et al., 2015; Karak, 2012; Montero de Espinosa and Meier, 2011; Zhang et al., 2015). Lot of studies have been presented to promote sustainability, and find alternate resource that can replace non-renewable resources with some renewable bio-derived alternative and use it for betterment of human society (Bhoyate et al., 2018c, 2017a,b; da Silva et al., 2018; Prociak et al., 2018a,b; Ranaweera et al., 2017a,b; Septevani et al., 2018; Zhang et al., 2017, 2018a). Soybean oil, orange peels oil and castor seeds oil are among some of the bio-sources largely used for the preparation of polyurethane foams (Gupta et al., 2014; Hejna et al., 2017; Ionescu, 2007; Javni et al., 2003). Industrial production for soybean, limonene, and castor oil creates an interesting potential for active producibility and use of such bio-based materials for polyurethane foams (Ionescu, 2007; Ranaweera et al., 2017a,b). Mercaptenized bio-based oils are another interesting sources for the preparation of polyurethane foams (Biresaw et al., 2017; Javni et al., 2016). Mercaptenized oils provide the advantage of thiol-ene reaction and possibility of several structural modifications leading to a wide range of physical properties to be used in different applications (Bhoyate et al., 2018b; Gupta et al., 2014; Ionescu et al., 2015; Ranaweera et al., 2017a,b).

High surface to volume ratio and hydrocarbon-based overall composition makes polyurethanes vulnerable to fire hazards (Bhoyate et al., 2018a,b; Ranaweera et al., 2017a,b; Zhang et al., 2018b). Small flint of fire could eventually grow in significant fire threat (Pan et al., 2015). In 2016, National Fire Protection Association estimates 1.34 million fires resulting in deaths of 3390 civilian, injuries to 14,650 civilians and direct property loss of about $10.6 billion (Haynes, 2017). Among them, fatal deaths of 2950 civilians, injuries to 12,775 civilians, and loss worth $7.9 billion to the property was due to structural fire. Rigid polyurethane foam is one of the important construction material used as thermal insulation in-house, furniture, vibration insulator, electrical insulation and in different industrial and household packings (Bhoyate et al., 2018b; Ionescu, 2007; Shea, 2005). Therefore, it is essential to develop efficient fire retardant rigid polyurethane foams which would prevent any type of fire hazards at the source.

Currently, two types of flame retardant materials such as additive and reactive are being used to prepare flame retardant polyurethane foams (Bhoyate et al., 2018b; Ionescu, 2007). Additive flame retardants

* Corresponding author at: Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762, USA.
E-mail address: rgupta@pittstate.edu (R.K. Gupta).

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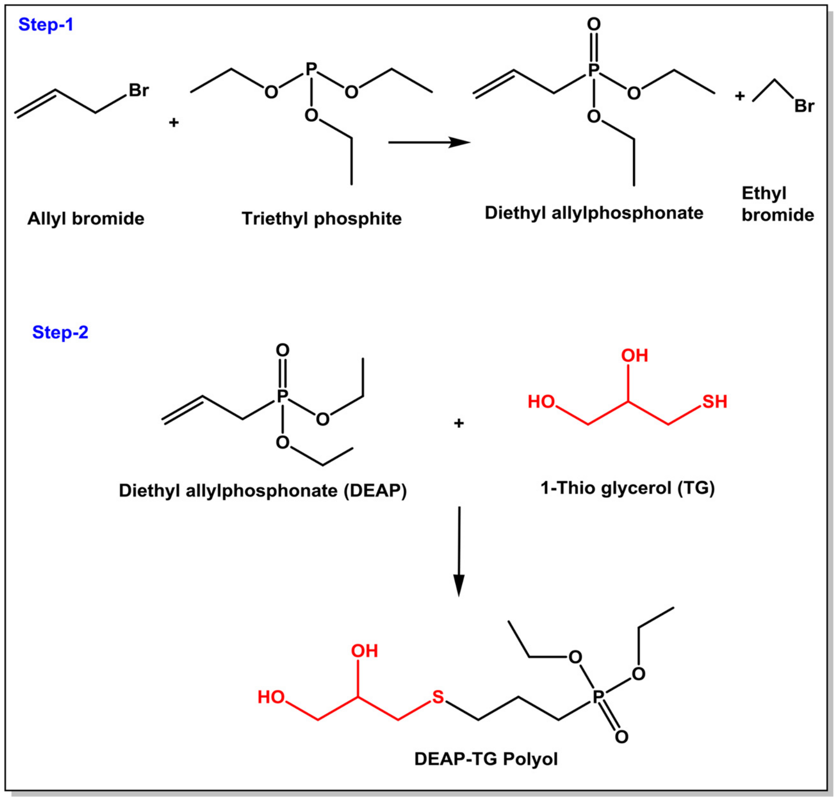

Fig. 1. Reactions for the synthesis of DEAP-TG polyol.

are suspended in the matrix of the foam during preparation to provide flame retardancy. However, they show the possibility of chronological migration compromising fire retardancy over time (Ionescu, 2007). Many studies based on halogenated and non-halogenated additive/reactive flame retardants were reported (Wu et al., 2013; Xing et al., 2013; Zhang et al., 2013a,b,2014). Tris (2-chloroisopropyl) phosphate and tris (1, 3-dichloroisopropyl) phosphate are two well-known liquid flame retardants from halogenated phosphorus flame retardant group, used in polyurethane foams (Gharehbagh and Ahmadi, 2012). The study suggests that addition of these flame retardants decrease the total heat evolved, but increase the smoke and carbon monoxide production. Reports for other additive-based flame retardants such as dimethyl methyl phosphonate, melamine, EG, N-(P,P'-diphenyl) phosphorus-based-(3-triethoxysilicon) propylamine (DPTP), aluminum hydroxide and magnesium hydroxide also exhibit a significant effect on the physical structure and mechanical properties of the foams (Chen et al., 2014; König et al., 2008; Ranaweera et al., 2017a,b; Zhang et al., 2013a,b). Hence, the use of reactive flame retardants having rigidly bonded chemical structure is preferred that would eliminate all the drawbacks affecting physical and mechanical properties. Our previous study of reactive halogenated flame retardants showed the improved mechanical behavior of the foam with increased addition of flame retardant polyol (Bhoyate et al., 2018b). However, it was observed that bromine (Br) based flame retardants need 5–6 wt% of Br concentration in foams to show better flame retardant characteristics. Compared to halogens, non-halogenated compounds based on phosphorus require lower concentration to provide better flame retardancy and improved physico-mechanical properties (Ionescu, 2007). For example, Zhang et al. have synthesized castor oil based flame retardant polyurethane foams by reaction of epoxidized castor oil with diethyl phosphate (Zhang et al., 2014). About 3% of phosphorus in the foam was reported to have 10% reduction in peak heat release rate as compared to the neat foam. Lignin-based reactive flame-retardant foams were synthesized using lignin-phosphorus polyol and additive microencapsulated phosphorous-based flame retardant (Xing et al., 2013). About 3% of phosphorus-containing foam was synthesized using 30% lignin and 15% microencapsulated flame retardant which showed 58% reduction in peak heat release rate. Hence, considering all the aforementioned criteria's, reactive flame retardant polyol based on phosphorus was studied to provide flame retardancy and smoke suppression to polyurethane foam.

In this study, a novel flame retardant polyol based on diethyl allyl phosphonate (DEAP) and thioglycerol (TG) was synthesized and used along with different bio-based polyols to prepare flame retardant rigid polyurethane foams. Bio-based polyols were derived from soybean oil, orange peel oil, and castor oil. Effect of phosphorous content from reactive flame retardant polyol on physicomechanical properties of the polyurethane foams was studied. Our results suggest that small amount of phosphorous based reactive polyol (1.5 wt% P in the foam) could significantly reduce the flammability while maintaining physico-mechanical properties of the polyurethane foams.

2. Experimental details

2.1. Materials

Castor oil (CO), limonene dimercaptan (LDM), mercaptanized castor oil (MCO) and mercaptanized soybean oil (MSOY) were purchased from Chevron Philips, USA. Triethyl phosphite, limonene (LIM), glycerol-1-allyl ether (GAE), 2-mercaptoethanol (ME) and thioglycerol (TG) were purchased from Acros Organic, USA. High oleic soybean oil (HOSO) was obtained from Archer Daniels Midland (ADM) Company, USA. Allyl bromide, 2-hydroxy-2-methylpropiophenone and Ni (II) acetylacetonate were purchased from Sigma-Aldrich, USA. Allyl alcohol (AA) was purchased from Alfa Aesar, USA. Jeffol SG-360, a sucrose-based polyether polyol and methylene diphenyl diisocyanate (MDI, Rubinate M isocyanate) were purchased from Huntsman, USA. DABCO T-12 and NIAX A-1 were obtained from Air Products and OSi