



The study of mechanical behavior and flame retardancy of castor oil phosphate-based rigid polyurethane foam composites containing expanded graphite and triethyl phosphate



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ABSTRACT

The goal of this work was the synthesis of novel flame-retarded polyurethane rigid foam with a high percentage of castor oil phosphate flame-retarded polyol (COFPL) derived from renewable castor oil. Rigid flame-retarded polyurethane foams (PUFs) filled with expandable graphite (EG) and diethyl phosphate (TEP) were fabricated by cast molding. Castor oil phosphate flame-retarded polyol was derived by glycerolysis castor oil (GCO), H_2O_2 , diethyl phosphate and catalyst via a three-step synthesis. Mechanical property, morphological characterization, limiting oxygen index (LOI) and thermostability analysis of PUFs were assessed by universal tester, scanning electron microscopy (SEM), oxygen index testing apparatus, cone calorimeter and thermogravimetric analysis (TGA). It has been shown that although the content of P element is only about 3%, the fire retardant incorporated in the castor oil molecule chain increased thermal stability and LOI value of polyurethane foam can reach to 24.3% without any other flame retardant. An increase in flame retardant was accompanied by an increase in EG, TEP and the cooperation of the two. Polyurethane foams synthesized from castor oil phosphate flame-retarded polyol showed higher flame retardancy than that synthesized from GCO. The EG, in addition to the castor oil phosphate, provided excellent flame retardancy. This castor oil phosphate flame-retarded polyol with diethyl phosphate as plasticizer avoided foam destroy by EG, thus improving the mechanical properties. The flame retardancy determined with two different flame-retarded systems COFPL/EG and EG/COFPL/TEP flame-retarded systems revealed increased flame retardancy in polyurethane foams, indicating EG/COFPL or EG/COFPL/TEP systems have a synergistic effect as a common flame retardant in castor oil-based PUFs. This EG/COFPL PUF exhibited a large reduction of peak of heat release rate (PHRR) compared to EG/GCO PUF. The SEM results showed that the incorporation of COFPL and EG allowed the formation of a cohesive and dense char layer, which inhibited the transfer of heat and combustible gas and thus increased the thermal stability of PUF. The enhancement in flame retardancy will expand the application range of COFPL-based polyurethane foam materials.

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1. Introduction

Rigid polyurethane foams (RPUF) that are an interesting family of polymers, with excellent thermal insulation, electrical insulation, chemical resistance and toughness combined with good low-temperature flexibility, are extensively used in insulation in refrigerators, construction materials, chemical pipelines [1,2], thermal insulation, space filling and other applications due to its excellent properties such as closed-cell structure, low thermal conductivity, low moisture permeability and high compressive

strength. However, RPUF are highly flammable and susceptible to degradation upon exposure to elevated temperature during fire accident, which constitutes a serious concern and restricts its application. Numerous studies have aimed to improve the fire behavior and thermal stability of RPUF.

One of the problems facing polyurethanes nowadays is their dependence on petroleum derivative products. In particular, polyurethanes, offering a broad variety of properties that are useful in different areas of applications, are very interesting materials that can be prepared from reactants obtained from renewable resources of wide availability. Due to oil crisis, governmental politics, global warming effects, legislation, economical factors and the growth of awareness towards environmental preservation, have led corporations and researchers to search for new processes, products and

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alternative raw materials in the polymer industry that minimize damage to the planet. New materials should have the same or better physical and chemical properties than those produced from petroleum; at the same time, the cost performance should also be compatible with commercial materials in the market. In the last years, the increasing interest in searching for a sustainable chemistry is promoting the replacing of petroleum derived raw materials with renewable raw materials in the production of polymers [3–5]. In this way, bio-based materials obtained from renewable resources are receiving considerable attention for an increasing amount of applications [6–9] from a social, environmental and energy standpoint, with the increasing emphasis on issues concerning waste disposal and depletion of non-renewable resources. Substitution of agricultural oils for petrochemically derived feedstocks in polyurethane synthesis has been an area of intense research and development for several decades. PU based on renewable resources has generated worldwide interest, especially development of vegetable oil based polyurethanes [10–12]. Among the natural oils, castor oil is an important renewable resource and widely used as a starting material for many industrial products [13].

In recent years, castor oil has attracted a lot of attention because of its wide possible applications. Castor oil is a renewable raw material that has been attracting research efforts due to its use in coatings, adhesives, paints, sealants, encapsulating compounds [14,15]. Researchers have been developing new types of polyurethane, using castor oil as a precursor for bio-polyurethane and polyurethane foams. Castor oil is an abundant and renewable natural resource available in large quantities from castor-oil plant seed; it is a kind of relatively low cost material which offers a priori possibility of biodegradation. Bio-based materials derived from castor oil are used to synthesize natural polyols, which are used as raw materials in the preparation of bio-based elastomeric polyurethanes. The unique feature of castor oil is that it contains considerable amount of hydroxylated triacylglycerols, which are important ingredients for polyurethane polymer. PU obtained from castor oil has certain disadvantages, including: low hydroxyl number leading to low modulus materials, a slower rate of curing of secondary hydroxyl groups [16] and low flame retardancy. The use of castor oil (CO) as polyol replacement in polyurethane formulations has been reported by several authors. However, the original concentration of hydroxyl reactive groups is not enough to obtain rigid PU. To offset these disadvantages, the chemical modification of castor oil is considered. Castor oil is transesterified or alcoholized with polyhydroxy alcohols, most commonly by glycerol, pentaerythritol, triethanolamine and trimethylol propane. Transesterification leads to an increase in hydroxyl value of the system thereby rendering hardness to the product, while long chain fatty acids induce flexibility. So transesterification is a possible route of modification to increase the hydroxyl groups in the oil structure [17]. The inflammability of PUF is due to the absence of information about the real structure of castor oil, which is a complex 12-hydroxy-9-cis-octadecenoic glyceride structure. The existence of ester group and alkyl makes it flammable. By considering these issues, it is necessary to improve the flame retardancy of PUFs that is realized through react with diethyl phosphate in order to evaluate their flame retardancy. In order to promote further utilization of castor oil in new fields of industrial products, it is crucial to control flame retardancy and hydroxyl value of products derived from castor oil. However, there is little study about castor oil-based flame-retarded polyols.

Since polyurethane foams are, in general, flammable materials, many efforts have been directed to improve their flame retardancy. However, the additive flame retardants are usually easy to separate out from PUF, especially for micromolecular liquid flame retardants, which decreases the permanent flame retardancy. Therefore, a

great deal of effort has been devoted to exploiting flame-retarded polyols for PUF, making the flame retardant element link to the PUF matrix by covalent bond. Polyurethane foam can be specifically modified in order to increase its flame retardancy by dispersing flame-retarded fillers and using modified polyols with flame retardant element such as halogen, phosphorus, nitrogen and silicon. Usually, the halogenated additives release corrosive, obscuring and toxic smoke, which pollutes environment, erode instruments, and even damages people's health. As a result, the flame retardant additives which have good flame retardant efficiency and hardly pollute environment are particularly needed.

Expandable graphite prepared from natural graphite by chemical treatment is a type of graphite intercalation compound. The excellent properties of expandable graphite kept most excellent characteristics of natural graphite and of its own, such as low price, overcame hard, abundance, permeability, electrical conductivity, increases of mechanical properties of polymers, high porosity and exchange surface, make it and its derivatives very useful as functional carbon materials that can be applied in various fields, such as conductivity polymer [18], airtight materials, oil absorbents, high-power batteries, electrodes, military materials [19,20], sealing, catalyzing mechanism, space flight military affairs, environmental protection etc. [21]. Another important property for expandable graphite is the flame retardancy. Some studies implied that EG could produce good fire-retardant properties for some polymers, such as polyolefins [22], polyurethane foam [23], coating [24], etc. In addition, EG after expansion can be used as biomedical materials due to its pore structure and absorptive capacity [25]. EG or modified EG is also another kind of typical flame retardant for a wide range of polymers, giving satisfactory fire retardancy in polyurethane. A number of studies have been conducted on expanded graphite-reinforced flame retardant polyurethane foams. This is because expandable graphite obtained by partial exfoliation, while being cheap, also has a high aspect ratio, and it forms a "wormlike" structure at high flame retardancy. EG is a structural modification of graphite obtained from intercalated [26] or oxidized [27] graphite via thermal reduction. This treatment of the graphite results in a light worm-like structure. When exposed to a heat source, EG, occupies hundred times its initial volume and generates a voluminous structure, thus providing fire-retardant performance for the polymeric matrix [28]. The special layer structure of EG is treated with sulfuric acid, nitric acid or acetic acid, which are intercalated into the graphite crystal structure. As to the origin of the flame retardancy of EG, it has been established that a "worm-like" structure layer can be formed on the surface of the materials due to the expansion of EG during burning, and such a layer of graphite can prevent heat and oxygen entering the bulk [29], thus providing fire resistance to the polymeric matrix. Lower size EG particles led to lower volume expansion ratio and less flame retardant efficiency [30]. Because the boiling point of graphite is above 3000 °C, EG can maintain its integrity in the flame zone and provide better fire protection than many other flame retardants. EG acts mainly in the condensed phase as a smoke suppressant and an insulator. If the expanded carbon layers are too unstable, EG needs to be combined with other flame retardants such as TEP to form stable intumescent layers.

In the present work, castor oil phosphate flame-retarded polyols were synthesized and we chose commercial expandable graphite and TEP in order to ensure flame retardancy of polyurethane foam. Mechanical property, morphological characterization, limiting oxygen index and thermostability analysis of PUFs were assessed by universal tester, scanning electron microscopy, oxygen index testing apparatus, cone calorimeter and thermogravimetric analysis. It reveals that polyurethane foam prepared from COFPL, EG and TEP exhibits high LOI, excellent thermostability and mechanical property.

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