European Polymer Journal 87 (2017) 209–220

Contents lists available at ScienceDirect

European Polymer Journal

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

Phosphorus containing castor oil based derivatives: Potential non-migratory flame retardant plasticizer

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ARTICLE INFO

Article history:
Received 10 October 2016
Received in revised form 17 December 2016
Accepted 19 December 2016
Available online 24 December 2016

Keywords:
Plasticizer
Castor oil
PVC
Migration

ABSTRACT

Sustainable resources, environment and health concerns, related to migration, toxicity and flammable problems from petroleum based plasticizer such as DOP, can be minimized by the use of phosphorus containing castor oil based derivative with zero migration and containing flame retardant groups. In the present study, we developed a novel phosphorus containing castor oil based derivative: propargyl ether EAMR-DOPO, which was covalently linked bound to the PVC-N_3 as an internal plasticizer. The obtained PVC materials exhibited more thermal stable at around 350–500 °C and lower *T*g than PVC. No migration was found in the migration stability tests. The method provided a general method for preparing non-migratory and flame retardant plasticizer derived from vegetable oil.

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1. Introduction

Poly(vinyl chloride), better known by its abbreviation PVC, is one of the most widely used economically relevant thermoplastic materials. It is the second largest manufactured resin around the world, applications in construction materials, children toys, food packing, medical tubing, blood bags, credits cards, wall papers, wire and cables, bottles and so on [1–5]. Production per annum of PVC resin has been exceeded 31 million tons since 2010 [6]. In order to obtain PVC materials with requirements in flexibility, a large amount of plasticizers were cooperated to make PVC easy process. The most common used plasticizers are phthalates, which account for more than 80% the entire plasticizer industry by volume worldwide [3]; 90% of plasticizers used in China are phthalate plasticizers [5,7]; because phthalates are low in price and high in plasticizing effect. However, the following reasons limit the wide range of applications of phthalates. First, the low molecular weight and degree of branching make phthalates easy migrate from PVC materials by volatilization or solvent extraction in acid solution, alkali solution, organic solvent or olive oil [7,8]. On the one hand, the loss of plasticizer changes the physical and chemical properties of PVC materials with the extent of time, and shortens their working life. On the other hand, phthalates were found possible toxic and biological effect on human body when the plasticizers were transferred to human [5,9,10]. Therefore, phthalate plasticizers have been restricted in medical devices, children toys and food packing with laws in European Union, the United States, and Canada [11,12]. Second, flammability of phthalate plasticizers makes them hard to be used in PVC products with high fire protection requirements. Last but not least, all of the phthalate plasticizers derived from petroleum

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http://dx.doi.org/10.1016/j.eurpolymj.2016.12.023
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resources. With the gradual depletion of petroleum resources and rising of petroleum oil price, the petroleum resources based chemical industry is unsustainable.

Recently, the use of vegetable oil as an alternative to petroleum-based raw materials for the designed and synthesized monomers have been paid particular attention due to the environment and economic concerns. Reactive diluents have been synthesized from cardanol oil for epoxy resin [13]. Biodegradable multifunctional additive derived from soybean oil for eco-friendly lubricant was also prepared [14]. Bio-based polyurethane materials have been synthesized from vegetable-oil-based polyol [15–17]. The resorbable biomaterials has, epoxidized alkyd resins and high-functionality unsaturated ester macromonomer were also prepared from vegetable oil [18–20]. Triacylglycerols are the main chemical structure of vegetable oil. The main components of triglyceride are saturated and unsaturated fatty acids, which have been used as platform chemicals for preparation of vegetable oil based plasticizer and experienced fast development [21]. In particular, epoxidized vegetable oil as environmental plasticizer was paid more attention, epoxidized soybean oil [22–23], epoxidized sunflower oil [24], epoxidized safflower oil [25], epoxidized linseed oil [26], epoxidized cottonseed oil [27], and epoxidized cardanol diethyl phosphate [28] have been reported. Epoxidized soybean oil has been used as commercial plasticizer for PVC materials because of excellent water resistance and oil resistance, while the epoxidized vegetable oil is a good auxiliary stabilizer which has a synergistic effect on PVC blended with organic tin and metal soap stabilizer [29]. The use of epoxidized vegetable oil as an alternative to phthalate plasticizers presented a good prospects for development, but the flammability of epoxidized vegetable oil, just as phthalate plasticizers, makes them hard to be used in PVC materials with high fire protection requirements. Flame retardant element or group (such as phosphorus) containing vegetable oil based derivatives can be used as flame redundant plasticizer. The chemical structure of triacylglycerol and phosphorus components of phosphorus containing vegetable oil based derivatives make them gain flame retardant and plasticization effect on PVC materials. The reason is that they provide abundant carbon sources and acid sources during thermal degradation process, which further enhance flame retardancy by promoting formation of char residue [21,30]. Fig. 1 shows a series of phosphorus containing vegetable oil based derivatives. Fig. 1(a and b) present the chemical structure of diphenyl phosphine oxide containing sunflower oil based

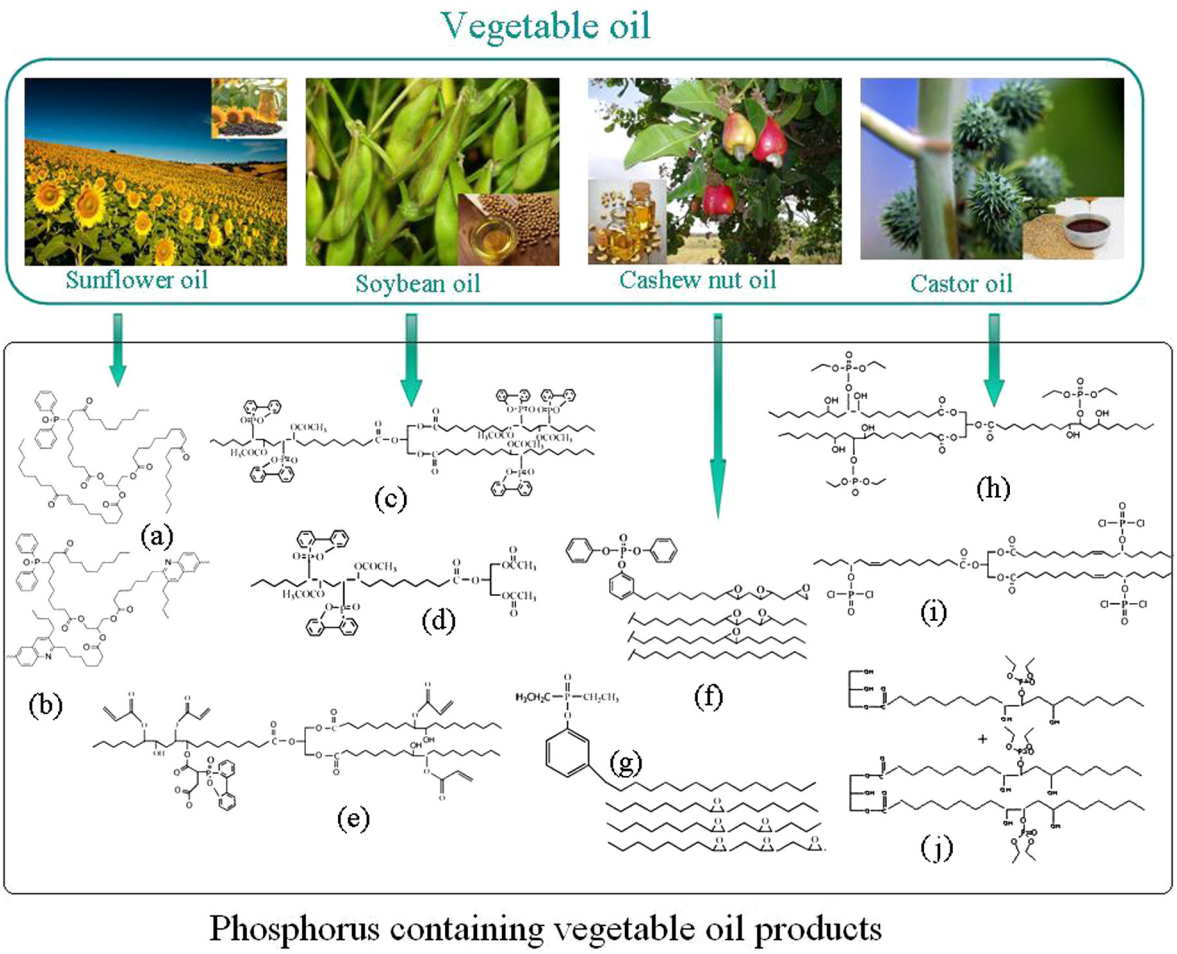

Fig. 1. Phosphorus containing vegetable oil products and their nature origin.

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