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A renewable waste material for the synthesis of a novel non-halogenated flame retardant polymer

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ABSTRACT

The recognition of toxicity and environmental persistence of halogenated flame retardant (FR) materials has prompted the reduction in their usage across the globe. There is an immediate need for new types of non-toxic and effective FR produced preferably through sustainable routes. Here we report the synthesis and characterization of a new polyphenolic FR material based on a renewable and biodegradable starting material, cardanol (a byproduct of cashew nut processing). Cardanol was polymerized in aqueous media using various types of oxidants. The thermal properties of the resulting polymers were investigated. Polycardanol synthesized using a specific type of oxidant exhibited good thermal stability and low heat release capacity. Preliminary results obtained from this study are quite promising and indicate the possibility of synthesizing new types of FR materials from bio-based phenols.

1. Introduction

1.1. Polymers and flame retardants (FR)

Polymeric materials have become an indispensable part of our daily life. The production and consumption of plastics is continuously increasing, due to their ability to conform to numerous applications. One of the major disadvantage of most polymeric materials is their intrinsic flammability (Lyon and Walters, 2004). This necessitates the use of external additives to ensure fire safety in most applications. Most polymeric formulations contain FR additives that decrease the rate of flame propagation through the material thus creating a less flammable product.

1.2. Toxicity of FR materials

Most FR materials used in polymeric applications are based on halocarbons, organophosphonates or metal oxides. Though some of these compounds impart excellent flame retardancy, they tend to be toxic (D'Silva et al., 2004) and persistent, having a significant long term impact on the environment (de Wit, 2002). It has been shown that some of the FR additives also emit toxic and corrosive gases during combustion. These FR additives and the products of their combustion threaten both air and water ecosystems (Alaee and Wenning, 2002). The presence of trace amounts of polybrominateddiphenylether (PBDE), (one of the widely used halogenated flame retardant) in sperm whales, seals, dolphins and even human beings (Birnbaum and Staskal, 2004), poses enormous environmental threats and health related issues throughout the world (Zarker and Kerr, 2008; Gutowski et al., 2005). While small molecule-based FR materials are effective in reducing flammability of polymers, they often leach out of polymeric products during use. This is one of the leading causes for the environmental toxicity and bioaccumulation of these FR materials (Grand and Wilkie, 2000).

1.3. Need for alternative FR materials through 'green' initiatives

With the European Union banning the use of halogenated FR (The European Parliament and the European Council, 2003; Gerrard and Kandlikar, 2007), there has been a tremendous need for new

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environmentally friendly, non-toxic, low-leaching alternative halogen-free FR polymers and additives. It is also important to establish ‘benign’ processing pathways in accordance with the principles of green chemistry, to produce cleaner products. Previous efforts dedicated for the synthesis of non-halogenated FRs were primarily on compounds containing phosphorus (Weil et al., 1999), silicon (Zaikov and Lomakin, 1998) and boron (Armitage et al., 1996). Simple co-polymerization of epoxies (Lin et al., 2000), vinyls (Liu et al., 1996) and acrylics (Banks et al., 1994) with phosphate monomers, linear polyphosphazenes and aromatic cyclic phosphazenes (Allen, 1994) are the broad categories of phosphorous containing non-halogenated FRs. Among silicon containing compounds, polymers based on linear silanes/siloxanes (Masatoshi and Serizawa, 1998) and silsesquioxanes (Provatas and Matisons, 1997) are being extensively investigated. Recently, polymers incorporating boric acid/borates (Morgan et al., 2000) and carboranes (Grimes, 1970) have been found to be very good non-halogenated FR materials. However, the starting materials and synthetic method used were toxic and the final product is also not environmentally benign (Lu and Hamerton, 2002). Hence, development of non-toxic alternatives to halogenated FR materials has been a priority for several organizations including the Toxic Use Reduction Institute (TURI).

1.4. Characteristics of FR materials

In polymers, flame retardancy is usually achieved by incorporating an additive that prevents flame propagation by physical (char forming or intumescent) and chemical (radical scavenging) action. On the other hand, polymers with excellent thermal stability such as Nomex™ can also be used directly in challenging fire-proofing applications.

1.5. Alternative phenolic FR materials

Phenols have been known to be very efficient radical quenchers and have been used extensively in the antioxidant industry. Polymers based on phenols (especially thermosets) have very high thermal stability and excellent char forming characteristics. These are important requirements for a good FR material (Bruno et al., 2001; Samuelson et al., 2000). Bio-derived and biodegradable phenols can serve as good, sustainable starting materials for the synthesis of FR polymers.

1.6. Cardanol

Cardanol (see Fig. 1) is a phenol with a meta-substituted C_{15} aliphatic chain and one of the main components of Cashew nut shell liquid (CNSL), a waste product from the cashew nut industry. Other important components of CNSL are also shown in Fig. 1. Biodegradability studies show that cardanol degrades to 96% of its original weight within 28 days (Evaluation Report on CNSL by Toxic Use Reduction Institute). Cardanol and its derivatives have been investigated for use in a variety of applications (Façanha et al., 2007). It has been reported that cardanol can also be used along with lignin-based compounds for the synthesis of polyurethanes that exhibit good thermal and mechanical properties (Minh Tan, 1996). The unsaturated chains of cardanol have been grafted with natural rubber to increase heat stability and the resulting compounds were reported to exhibit much better thermo-oxidative stability (Vikram and Nando, 2007). Derivatives of cardanol have also shown promise as anti-oxidants in the stabilization of gasoline (Dantas et al., 2003). CSNL derivatives have been brominated and the resulting products have been found to possess good FR behavior; however the inherent toxicity of brominated compounds limits the use of these materials in FR applications (Pillai, 2000).

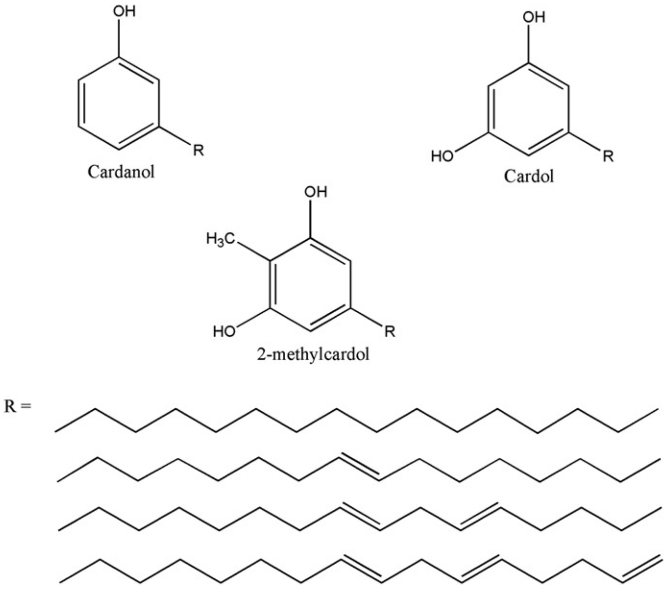

Fig. 1. Structures of the components in Cashew Nut Shell Liquid.

There have been several reports on the use of oxidative catalysts such as iron salen for the polymerization of cardanol (Ikeda et al., 2002). The reaction involved the use of a toxic biphasic organic reaction media (dioxane, dimethylformamide) (Kim et al., 2003; Won et al., 2004) to prevent the hydrocarbon tails from interfering with the polymerization reaction. The yields reported were also quite poor. One of the principles of green chemistry emphasizes the use of ‘renewable feedstock’ (Anastas and Warner, 1998; Uihlein et al., 2008). Another important aspect of greener chemical reactions is the utilization of water as the reaction media, especially for large-scale synthesis. In an attempt to adopt these principles in the design of new FR materials, oxidative polymerization of a renewable material (cardanol) has been explored in aqueous media.

2. Materials and methods

2.1. Materials

Cardanol and hydrogenated cardanol were obtained from Palmer International Inc (Skippack, PA). Potassium ferricyanide, ferric chloride, ammonium persulfate and sodium hydroxide were purchased from Sigma Chemicals Co. (St. Louis, MO).

2.2. Methods

In a typical reaction, cardanol (0.3 g, 1 mmol) was dissolved in 100 ml of water containing sodium hydroxide (2 g, 50 mmol) maintained at 50 °C. An oxidant such as potassium ferricyanide (0.658 g, 2 mmol) was then added to the solution and the mixture was stirred at 1100 rpm for 6 h. The polymer (brown solid) was filtered after salting out with sodium chloride (5.84 g, 0.25 mol) followed by extensive washing with water to remove any residual sodium chloride. The filtered product was then washed with hexanes in a Soxhlet extractor for 24 h to remove unreacted monomer. The reactions with hydrogenated cardanol were also carried out using the above described procedure. Control reactions were carried out at neutral pH or in the absence of oxidant. In

Table 1
Oxidative polymerization of cardanol in water. [All reactions were carried out under oxygen].

S.NO	Cardanol (mmol)	Oxidant (mmol)		NaOH (mmol)	Yield (%)
1	1	$K_3[Fe(CN)_6]$	5	0	0
2	1	$K_3[Fe(CN)_6]$	5	50	78
3	1	$K_3[Fe(CN)_6]$	2	50	74
4	0.1	$K_3[Fe(CN)_6]$	2	50	28
5	1	$(NH_4)_2S_2O_8$	2	50	0
6	1	$FeCl_3$	2	50	32

addition the type of oxidant and the oxidant to monomer ratio was varied (as shown in Table 1) to optimize product yield.

3. Results and discussions

The oxidative polymerization of phenolic monomers at high pH proceeds as shown in Fig. 2. The reaction can either proceed through a C–O–C coupling and/or through aromatic C–C linkages. High pH conditions are required for complete ionization of the phenol. The monomer can subsequently be polymerized using a strong oxidant. Alkaline pH is known to significantly decrease the oxidation potential of phenols (Saito et al., 2004). The polymerization of 2,6-dimethylphenol in water using oxidative catalysts has been previously reported (Saito et al., 2004).

Cardanol when dissolved in high pH water forms a dark pink colored solution. This solution can be oxidatively polymerized to a dark brown insoluble polymeric product using potassium ferricyanide. The polymer was isolated and characterized using Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectroscopy. The FTIR-ATR spectra of (a) cardanol and (b) poly (cardanol) are shown in Fig. 3.

The FTIR spectrum of the polymer shows characteristic peaks at 1240 and 1190 cm^{-1} which is attributed to vibrations of C(Ar)–O–C (Ar). The 1155 cm^{-1} peaks are attributed to C(Ar)–OH linkage. In comparison with the monomer spectra, there is also a large decrease in the intensity of the peak at 3400 cm^{-1} which corresponds to O–H vibrations. This may indicate the possibility of extensive C–O–C coupling. The spectrum of the polymer correlates very well with the IR spectra reported for poly(cardanol) (Ikeda et al., 2000). The use of hydrogenated cardanol in place of cardanol did not significantly change the spectroscopic properties of the final product formed. The use of other oxidants/catalysts such as ferric chloride [entry 5, Table 1] and ammonium persulfate [entry 6, Table 1] did not produce a polymer.

(The use of strong oxidants is not favorable from the environmental and toxicity standpoint, but this is a preliminary effort demonstrating the polymerization of a renewable starting material in an aqueous environment. With the success of this effort in producing a polymeric FR material based on cardanol, other greener, non-toxic oxidants or catalysts can also be explored for the synthesis.)

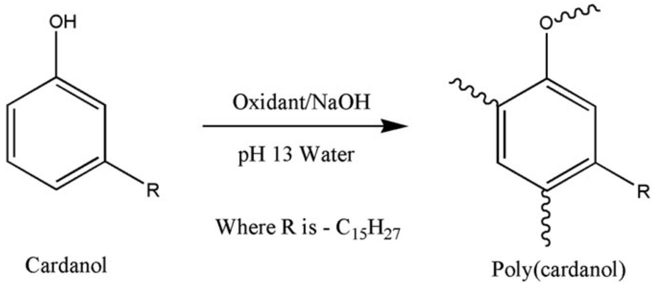

Fig. 2. Proposed reaction scheme for poly(cardanol) synthesis.

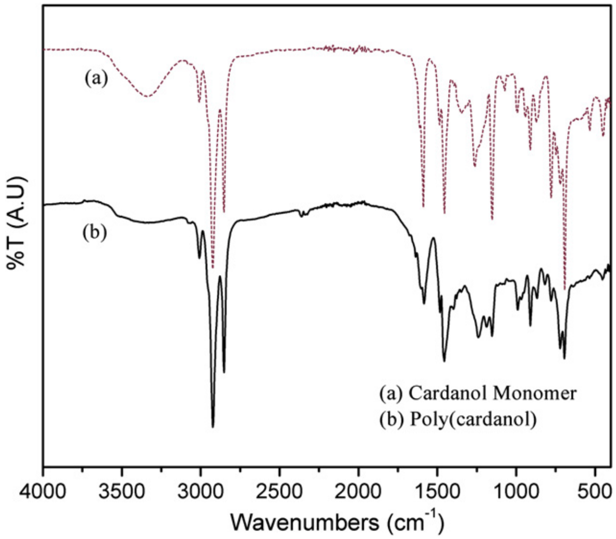

Fig. 3. FTIR-ATR analysis of cardanol monomer and poly(cardanol) synthesized using $K_3[Fe(CN)_6]$.

3.1. Thermal characterization

3.1.1. Thermogravimetric Analysis (TGA)

TGA studies were carried to assess the thermal stability and char forming capability of the synthesized poly(cardanol). TGA spectra of the monomer and the polymer were carried out in air at a heating rate of 20 °C min^{-1} Fig. 4 clearly shows that the poly (cardanol) has better thermal stability when compared to the cardanol monomer. In addition, the polymer forms reasonable amount of char after thermal degradation. The char accounts for about 25%

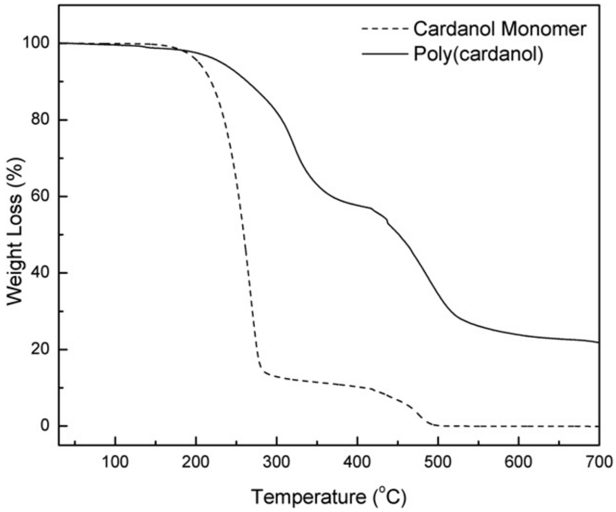

Fig. 4. TGA analysis of cardanol monomer and poly(cardanol) synthesized using $K_3[Fe(CN)_6]$.

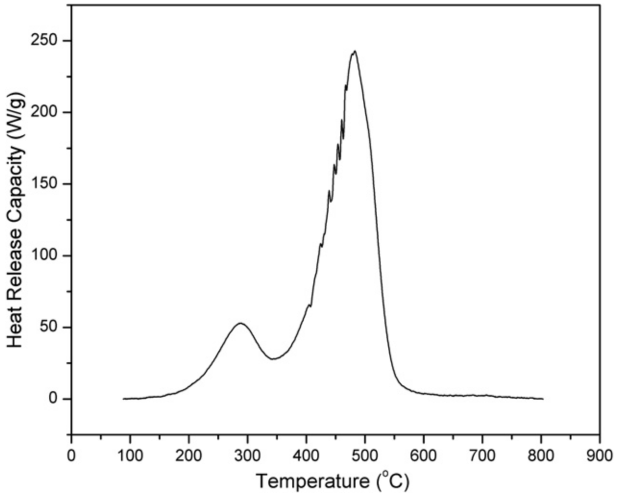

Fig. 5. PCFC analysis of poly(cardanol) synthesized using K_3 [Fe(CN)$_6$].

of the initial weight of the polymer at temperatures as high as 700 °C. For a good FR material, formation of reasonable amounts of char (upon thermal degradation/burning) is beneficial. The char can potentially inhibit flame propagation through the substrate by forming a physical barrier that cuts off the supply of oxygen required for combustion. Further, char layer also helps prevent diffusion of combustible polymer degradation products to the flame. The phenolic groups in the polymer can also act as radical traps and further prevent flame propagation. The insolubility of the final poly(cardanol) has impeded further detailed structural characterization.

3.1.2. *Pyrolysis flow combustion calorimetry (PCFC)*

PCFC is a technique that provides information about the rate of combustion of a material through heat release capacity (HRC) values. HRC is an important parameter useful in assessing the fire hazard of a material. PCFC analysis was done with 5 mg of the polymer sample with highest yields of the reaction product. The polymer was flash-pyrolyzed at 5 °C/sec to 1200 °C. Pyrolysis products (gaseous) were swept by an inert gas (nitrogen) into a combustion chamber containing oxygen. In the chamber, the ratio of N_2 to O_2 in the mixture was comparable to that present in atmospheric air. Heat release rate was calculated from the rate of consumption of oxygen. The percentage char at 760 °C was also calculated. Poly(cardanol) synthesized using potassium ferricyanide exhibited maximum heat release at a temperature of about 480 °C (Fig. 5) with reasonable char yields (22.6%) as shown in Fig. 4. The polymer also exhibited low HRC (285 J/g K) (Fig. 6).

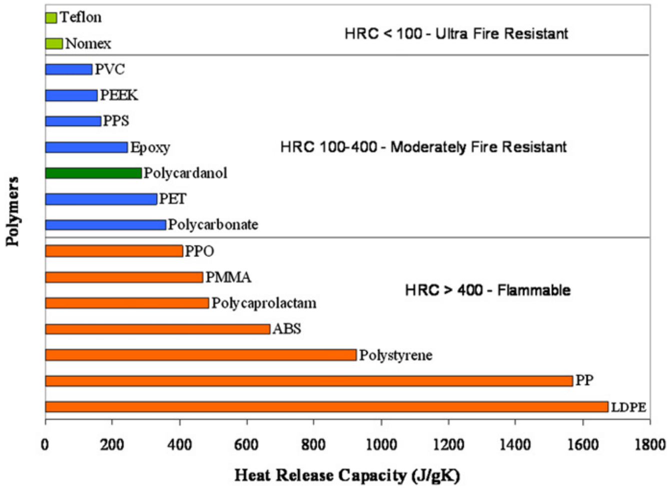

Fig. 6. PCFC Analysis of poly(cardanol) in comparison with commercial used polymers.

Fig. 6 shows the comparison of the HRC of poly(cardanol) with other commercially used polymers. These materials can be classified as moderately fire resistant according to classification of FR materials based on their HRCs as described by Walters and Lyon (2003).

4. Conclusions

The synthesis of a novel non-halogenated FR polymer based on a renewable and biodegradable starting material (cardanol) is reported. The reactions were carried out in aqueous media, without the use of organic solvents. The polycardanol clearly exhibited reasonable thermal stability and fairly low heat release capacity as substantiated by the TGA and PCFC results respectively. The use of a sustainably sourced starting material combined with a polymerization reaction that is carried out in aqueous media; provide opportunities for producing FR additives using cleaner processes. The amphiphilic nature of cardanol could also be utilized to design polymerization reactions in organized media and obtain well-ordered and perhaps more processable polymers. More efforts are underway to understand the mechanism of the polymerization and the nature of the product that can provide superior thermal and FR properties.

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