

Thermally Stable Polymers of Cardanol as Char-Forming Additives for Polypropylene

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ABSTRACT: Globally, certain types of halogenated flame retardant additives (FR) are becoming increasingly regulated or banned from being used in polymers. There is an immediate need for alternative non-toxic thermally stable polymers and char-forming additives. Development of non-halogenated FR for the commonly used and highly flammable thermoplastics, namely polyolefins, is particularly important and challenging. This research explores the possibility of utilizing char-forming compounds based on polymer of cardanol as an additive that can lower the heat release capacity (HRC) when blended with polypropylene (PP). Polycardanol is thermally stable and exhibits moderate HRC upon thermal decomposition and forms a significant amount of char. The use of a polymeric form of phenol eliminates any processing-induced decomposition problems. Here we report the synthesis and characterization of polycardanol as well as the thermal and rheological characterization of blends of polycardanol with PP. Pyrolysis Combustion Flow Calorimetry studies indicate that blending of polycardanol with PP can effectively lower the HRC by over 20%.

KEYWORDS: Polycardanol, polypropylene, polyphenols, flame retardant additives, thermal stability

1 INTRODUCTION

Flame retardants (FR) are one of the important classes of polymer additives that prevent or delay the initiation and propagation of fire in plastics and elastomers. Polyolefins such as polypropylene (PP) are especially very flammable and exhibit high heat release capacities (HRC) of around 1300 J/g-K. In these cases, FR additives and synergists are very crucial for ensuring fire-safety of products produced using these polymers. The design of organic FR additives suitable for PP is often a challenge due to the processing conditions (the FR material should not degrade during processing) and the high surface pyrolysis temperatures reached during combustion [1]. Halogenated compounds or phosphorus-based FR in combination with metal oxide synergists

are the most commonly used FR additives for PP. Mineral fillers like aluminum hydroxide, magnesium hydroxide, calcium carbonate and talc are also commonly used [2]. If used alone, for best results, mineral fillers must be added in high concentrations (> 25 weight %) to achieve good FR properties. This level of filler is often detrimental to the mechanical properties of the polymer. However, small amounts of mineral additives are useful as smoke suppressants in FR formulations for PP [3].

The toxicity and environmental persistence of halogenated compounds has led to the quest for the development of alternative non-halogenated FR. Halogenated FR can be slowly released from polymer matrices, making their way up the food chain and accumulating in humans [4]. Some types of halogenated FR (for example, hexabromocyclododecane and decabromodiphenyl ether) are now known to cause cancer and a number of serious non-cancer health effects, including damage to the immune, reproductive, nervous, and endocrine systems [5–8]. They also

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pose a serious environmental risk from secondary poisoning in the food chain, and there is concern about the exposure of infants to halogenated FR [9, 10]. Small molecule FR can slowly migrate to the surface of products and come in direct contact with skin, causing bio-accumulation in humans [11, 12]. In addition, there is a significant risk of fire toxicity with halogenated compounds, as they are known to generate toxic, corrosive gases during combustion [13, 14]. Due to these serious detrimental environmental effects and health-related issues of halogenated FRs, they are being phased out in many countries.

Hindered phenols and amines are very well-known antioxidants used in plastics and rubbers at concentrations of 1–2 weight percent [15–17]. They are efficient in trapping reactive radical species like $H\cdot$, $OH\cdot$, $R\cdot$ and $ROO\cdot$ (as shown in Figure 1) during oxidative or thermo-oxidative degradation of polymers. This may be analogous to the gas-phase flame (radical scavenging) action of many halogen-containing FRs, but is distinctly different in the reaction temperatures and the kinetics of the process. The burning process of PP involves an oxidative pyrolysis that leads to the formation of very combustible species that become the fuel. It was previously reported that the use of these antioxidants can interfere with this process and result in beneficial FR properties [14].

But these additives by themselves show only moderate flame resistance and had to be used in synergistic combinations with halogen- and metal-oxide-based systems to obtain reasonable FR characteristics in addition to antioxidant properties [18]. Further, FR additives are usually incorporated into plastics at higher loading levels compared to antioxidants and the use of antioxidants in such high volumes for flame retardancy is not economical. In order to be commercially viable, starting materials for the synthesis of new types of organic radical scavenging or char-forming additives should be abundantly available at a reasonable cost.

Polyphenols exhibit good thermal stability, low HRC and have good char-forming properties. Hydroxyl groups in a polymer have been known to

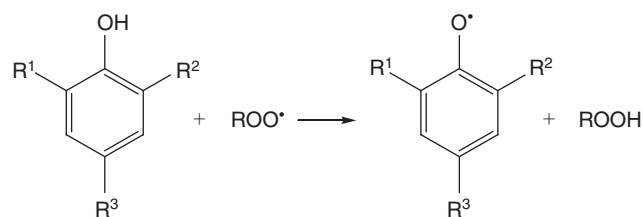


Figure 1 Antioxidant mechanism of sterically hindered phenols.

decrease the values of HRC, a quantitative predictor of polymer flammability [19]. The use of a polymeric system will eliminate the problems associated with leaching and bio-accumulation of small molecule-based FR. Further, upon thermal decomposition, polymeric phenols that have not degraded/been released into the flame can form a significant amount of carbonaceous char in the condensed phase. The char formed can also assist in quenching the flame by cutting off oxygen supply to the burning polymer. The char formation possibilities of polymeric phenols form the basis for exploration of their FR behavior in this paper.

There are numerous natural sources of polyphenols. It has been reported that lignin can enhance the thermal stability, char formation, and suppress the flammability in many polymers such as PP and poly(butylene succinate) [20–23]. The highly complex structure of lignin also increases aromatic char formation in the condensed phase [24]. However, the complexity of lignin's structure, very high molecular weight, low processability, poor blend compatibility, and the poor mechanical and rheological properties of the blend have prevented its widespread use [25, 26]. A naturally occurring phenol monomer such as cardanol can be used as the starting material for the synthesis of oligomers/polymers with potential utility in stabilizing commodity plastics.

Cardanol is a phenol with a meta-substituted C_{15} aliphatic chain (Figure 2) and is one of the main components of cashew nutshell liquid (CNSL), a biodegradable waste product from the cashew nut industry. Cardanol and its derivatives have been used for decades in a variety of applications as thermosets, mainly as a replacement for phenol [27–29]. Cardanol-based thermosets have high thermo-oxidative stability and are often used in industrial brake systems and friction lining in automobiles [30]. This renewable monomer can be a low cost starting material for the synthesis of fine and functional molecules such as surfactants, coatings [31, 32] and also polyphenol-based FR. Additionally, the long aliphatic side chains also offer the possibility of creating reasonably compatible blends upon blending with PP.

Polycardanol can be synthesized using chemical and enzymatic methods [33–35]. We have recently reported the synthesis of polycardanol using

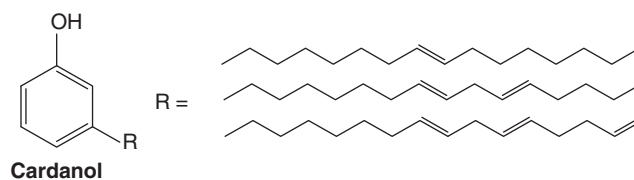


Figure 2 Chemical structure of cardanol.

potassium ferricyanide as the oxidant [36]. Here we report the scale up of the chemical synthesis of polycardanol and study the thermal properties of blends of polycardanol in PP.

2 EXPERIMENTAL

2.1 Materials

Technical grade cardanol was obtained from Palmer International (Skippack, PA). Potassium ferricyanide ($K_3[Fe(CN)_6]$ – purity: 98%) was purchased from Acros and used as oxidant. Sodium hydroxide (NaOH – purity: 97%) and two types of commercial halogenated FR including Decabromodiphenylether (DBDPE – purity: 98%) and Hexabromocyclododecane (HBCD – purity: 95%), were purchased from Sigma-Aldrich. All additives and solvents such as hexanes from Pharmco-AAPER (purity: 99.5%) were used as received without further treatment. Polypropylene homopolymer (PP – grade RJ470MO) with melt flow index (MFI – 2.8 g/10 minutes at 190°C) was purchased from Borealis. All blends reported in this paper were prepared by compounding additives into this polypropylene resin.

2.2 Synthesis of Polycardanol

Polycardanol was synthesized from cardanol by a variation of the synthetic procedure reported by us elsewhere [35, 37]. In the scale-up reaction, 10 grams of cardanol were dissolved in 2.5 liters of sodium hydroxide solution (containing 40 grams of NaOH in 2.5 liters of water) maintained at pH 13 and a temperature of 55°C. This dark pink colored solution was oxidatively polymerized to form a dark brown insoluble product using 22 grams of $K_3[Fe(CN)_6]$ as the oxidant with constant stirring for 6 hours. The reaction can either proceed through a C-O-C coupling and/or through aromatic C-C (ortho and para) linkages as

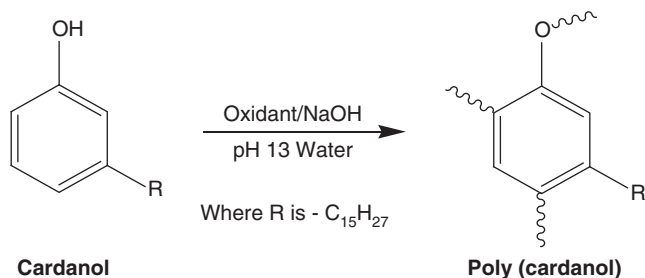


Figure 3 Chemical oxidative polymerization of cardanol using potassium ferricyanide.

shown in Figure 3. The polymer product precipitated out from the solution. The precipitate was filtered and washed with deionized water (60°C, 500 ml each time) for three times to neutralize the product. Soxhlet extraction was carried out in hexanes for 24 hours to remove unreacted monomer. After drying the product, it was ground in a modified nut blender into micron-sized particles. This ground powder was blended with PP according to the procedure described in the following section.

2.3 Blending of Polycardanol and Halogenated FR into PP

Polycardanol was compounded with PP using a C.W. Brabender Type 6 Mixer with counter-rotating screws. The compounding process was optimized using virgin PP. The barrel temperature and mixing time were fixed such that the base resin is molten but does not degrade during the compounding process. The barrel was maintained at a temperature of 195°C. Optimized rotor speed was 60 rpm and the total compounding time was set to 10 minutes for the preparation of all blends. Additives were added to the compounder after complete melting of PP, two minutes after the compounding process was started. Additive loading of 1, 5, 10 and 15% by weight were used with respect to the weight of the base PP resin. For the sake of comparison, blends of PP with two commercially available halogenated flame retardants, namely DBDPE and HBCD, were also prepared using the same procedure.

2.4 Characterization of Polycardanol and PP-Polycardanol Blends

2.4.1 Spectroscopic Characterization

Polycardanol is insoluble in most common organic solvents. Hence structural characterization was limited to techniques that can accommodate solid samples. Fourier transform infrared (FTIR) spectroscopy measurement was carried out on a Thermo Scientific Nicolet 4700 FTIR with a smart orbit Attenuated Total Reflectance (ATR) accessory. Vacuum dried polymer samples were used for this purpose. The poor solubility of polycardanol prevented further characterization using nuclear magnetic resonance spectroscopy (NMR) in solution.

2.4.2 Thermal Characterization

a. Thermal Degradation Studies

Thermogravimetric analysis (TGA) of samples was done using a TGA Q 50 under nitrogen or

air purge of 10 ml/min to study the thermal stability of materials. Approximately 10 milligrams of samples were weighed and heated from room temperature to 750°C at a constant heating rate of 20°C/min. Multiple runs were carried out for each sample to ensure consistency of the results.

b. Heat Release Capacity Measurement Using Pyrolysis Combustion Flow Calorimetry

Pyrolysis combustion flow calorimetry (PCFC) or micro-scale combustion calorimetry was performed using a FAA micro calorimeter from Fire Testing Technology Limited to predict polymeric flammability in terms of total heat release (THR) and heat release capacity (HRC). Samples were heated at 1°C/sec to 750°C until decomposition was completed. Typically, 5 mg of sample was used for the test. All tests were done in triplicate and the results were averaged. For blends of PP with polycardanol, the samples were cut out from different portions to ensure that the results are representative of the actual blend and any variation caused due to heterogeneity is substantially minimized.

c. Mechanistic Study of Thermal Degradation Using Evolved Gas Analysis

Evolved gas analysis (TGA-FTIR) was used to monitor the degradation products of samples. In the experiment, TGA equipped with a N₂ gas purge was connected with a TGA-FTIR interface (Thermo Electron Corporation) which was installed in the infrared spectrometer. The nitrogen gas was set as 50 ml/min for its flow rate. The sample was run under nitrogen at a heating rate of 20°C/min from room temperature to 750°C. The temperature at transfer pipe was set at 215°C while the TGA-FTIR sample cell was set at 245°C to prevent condensation of volatiles. Gram-Schmidt chromatogram was used to exhibit the total infrared absorbance of volatiles as a function of time. The data from infrared spectrometer was composed of a series of IR spectra measured at an average of 16 scans with 4 cm⁻¹ resolution. Four spectra were obtained every minute. GRAMS/3D (FTIR spectra as function of time) graphs were also plotted to explain the evolution of gaseous products.

2.4.3 Rheological Behavior Analysis

Dynamic shear measurements of all blends were done using an ARES rheometer (TA Instruments) equipped with parallel plate fixture (25 mm) diameter plates at 210°C in the frequency range of 0.1 to 500 rad/s.

3. RESULTS AND DISCUSSION

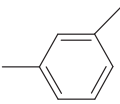
Radical scavenging and char formation are widely accepted strategies for imparting flame retardant characteristics to polymers. Naturally occurring phenols (such as cardanol) are a renewable source for synthesizing radical scavengers and char formers that can also be compatible with polyolefins. Beyond sustainability implications, the justification for the selection of cardanol as the starting material for this study also resides in the possible inherent compatibility with PP.

Theoretical basis for expected compatibility of polycardanol with PP: The solubility parameter of polycardanol was calculated using the Small & Van Krevelen method [38]. For calculating the solubility parameter of polycardanol a few assumptions were made. First the calculation was only carried out for a trimer. Depending on whether the polycardanol is C-C coupled/ C-O-C coupled or a combination of C-C and C-O-C coupled, the estimated values are in the range of 9.45 and 9.75 (cal cm⁻³)^{1/2} as shown in Table 1. The reported solubility parameter of PP ranges from 7.9 to 9.4 (cal cm⁻³)^{1/2} [39]. The presence of the long aliphatic *m*-substituted side chains in polycardanol can provide reasonable compatibility with PP. We therefore conclude that polycardanol can be used as an additive for polyolefins.

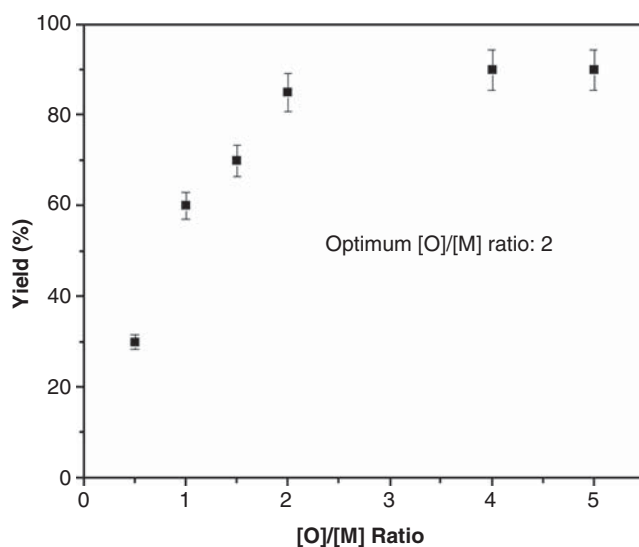
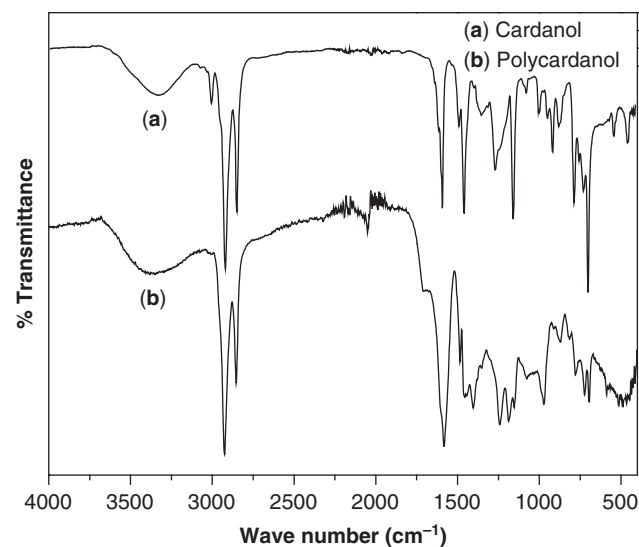
Scaling-up the synthesis of polycardanol: Commercial success of any FR additive as a potential replacement for halogenated FR is only possible if the raw materials are easily available at a low cost and the reaction is scalable to large volumes at a reasonable cost. Polycardanol was synthesized in the scale of 10 grams per batch in a lab-scale reactor. Figure 4 shows the optimization of oxidant/monomer ratios ([O]/[M]) in 5 liter reactor vessels for the synthesis of polycardanol. A maximum yield of 87% was attainable for reactions with [O]/[M] ratio of 2. Further increase in oxidant amount did not significantly affect the final yield of these reactions.

Characterization of polycardanol: As mentioned earlier, a major limitation in characterizing polycardanol is its insolubility in most organic solvents. This has prevented extensive structural characterization of the products using well-established methods such as NMR. Polymers of *p*-cresol synthesized using potassium ferricyanide as oxidant have been reported to yield insoluble products, characterized predominantly by FTIR spectroscopy [40]. Figure 5 illustrates the FTIR-ATR spectra of polycardanol synthesized using K₃[Fe(CN)₆] in comparison with cardanol monomer. The peaks at 1240, 1190 and 1155 cm⁻¹ are attributed to vibrations of C(Ar)-O-C(Ar) and C(Ar)-OH linkages. In comparison with the monomer spectra, there is also a decrease in the intensity of the peak at 3400

Table 1 Solubility parameter of polycardanol calculated using Van Krevelen molar attraction constants.

Polymer	ρ (g cm ⁻³)	F [(cal cc) ^(1/2) mol ⁻¹]	δ (cal cm ⁻³) ^{1/2}
Polycardanol (Trimer)	0.97	730	9.75
			C-C coupled
		—OH	9.45
		—O—	9.65
			C-O-C coupled
			C-C + C-O-C

ρ : density, F: molar attraction constant, δ : solubility parameter

**Figure 4** Optimization of oxidant/monomer ratio in 5L reactor for polycardanol synthesis using $K_3[Fe(CN)_6]$.**Figure 5** FTIR-ATR spectra of cardanol and polycardanol synthesized using $K_3[Fe(CN)_6]$.

cm⁻¹ which corresponds to O-H vibrations. This may indicate the possibility of extensive C-O-C coupling.

Another important change (as shown by the FTIR spectra in Figure 5) when the reaction was scaled up is the level of unsaturation of the polycardanol. We have reported earlier that when the [O]/[M] ratio was around 1, the FTIR peak at 3010 cm⁻¹ corresponding to C=C-H stretching remains unaltered (when going from a monomer to the polymeric state), suggesting no undesirable crosslinking reactions [35]. However, the FTIR-ATR spectrum of polycardanol when the reaction was scaled up with [O]/[M] ratio of 2 shows the disappearance of 3010 cm⁻¹ peak (unsaturated hydrocarbon moieties). This may be due to the crosslinking of the double bonds in cardanol. Additionally, the polymer exhibits a small peak at 1660 cm⁻¹ due to

C=O stretching from carbonyl groups. This indicates possible oxidation of the cardanol under alkaline conditions.

Thermal stability: The thermal stability and char-forming capability of polycardanol synthesized using $K_3[Fe(CN)_6]$ were evaluated by TGA. Figure 6 clearly shows that polycardanol has better thermal stability than cardanol monomer in both atmospheres. Under nitrogen, polycardanol exhibits two-step decomposition centered at 245°C and 460°C with 17% char remaining at 750°C. It is predicted that the first step in the degradation is due to the decomposition of the unsaturated aliphatic side chains, which accounts for roughly 15% of the total polymer weight. Subsequent degradation accounts for 40% weight loss and is attributed to decomposition of -OH entities and C-O-C

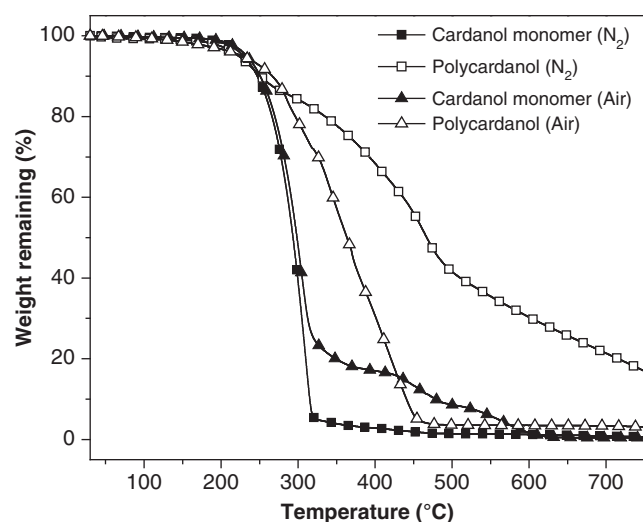


Figure 6 TGA thermogram of cardanol monomer and polycardanol synthesized using $K_3[Fe(CN)_6]$.

linkages [41]. For TGA thermogram of polycardanol under air, two-step decomposition is also observed at around 290°C and 370°C. However, the char remaining at 750°C is decreased to 3%.

Heat release capacity and heat release rate: The PCFC micro-scale test was designed by Lyon *et al.* to measure the heat release capacity of polymers [42]. In a PCFC, the sample is heated using a linear temperature program in a nitrogen atmosphere and the volatile decomposition products are swept from the pyrolysis chamber by an inert gas and combined with excess oxygen in a furnace at flame temperatures to force complete combustion (oxidation). Time-integration of the PCFC heat release rate (HRR) gives heat of complete combustion/oxidation, and the char yield is measured by weighing the sample before and after the test. The PCFC can also estimate the maximum amount of heat released by the sample per unit mass per degree of temperature change (J/g-K), also known as heat release capacity (HRC). The HRC of a polymer is an intrinsic material property and can be related to flammability [43]. Even though HRC is an excellent fire performance predictor, it does not directly account for the effects of swelling, dripping and barrier formation during the combustion of a polymer, all of which are essential parameters for flame quenching. The PCFC results of polycardanol (as shown in Table 2) indicate moderate HRC in a range of 320–330 J/g-K (most materials having HRC less than 300 J/g-K are considered having low HRC according to reports by Lyon *et al.* [44, 45]). The actual HRR versus temperature curves for polycardanol obtained using PCFC is provided in the supplementary information S1.

Table 2 Summary of PCFC analysis of PP/Polycardanol blends.

Polymer	THR (KJ/g)	HRC (J/g-K)	% Decrease in HRC
Polycardanol (PC)	25.4	326	–
PP	40.6	1288	–
PP + 1PC	42.5	1151	9.8
PP + 5 PC	39.7	1100	14.6
PP + 10 PC	39.7	1056	18.0
PP + 15 PC	37.8	986	23.4

3.1 Blends of Polycardanol and Polypropylene

3.1.1 Thermal Stability of Blends

Thermal decomposition temperature (T_d) of PP/Polycardanol blends were calculated from the TGA thermograms shown in Figure 7(a) using a step transition function in TA Instruments Universal Analysis software. Virgin PP used in this study has a T_d of 463°C. Polycardanol-PP blends show an appreciable increase in the temperatures at which T_d occurs and a marginal increase in char-forming capability. At 10% polycardanol loading, there is a 36°C increase in T_d . However, beyond 10% additive loading there is phase separation in these blends resulting in deterioration of the blend properties, evidenced by lower T_d for 15% loading in comparison to 10% loading. From Figure 7(b) it is obvious that under nitrogen, although the decomposition temperatures for the blends are higher, the rate of degradation of the blends is similar or higher than virgin PP. The polycardanol appears to function as filler that substantially increases the thermal degradation temperature but not the rate of degradation in nitrogen atmosphere.

3.1.2 Evolved Gas Analysis

A combination of thermogravimetric analysis and Fourier-transform infrared spectroscopy (TGA-FTIR) can be a useful tool for the possible determination of the degradation pathway of polymers, and the influence of FR additives on the degradation pathway. This tool has been previously used to monitor the degradation of several polymeric systems like polystyrene and polymethylmethacrylate [46]. From the Gram-Schmidt curves, the evolution of gaseous products (volatiles) during the thermal decomposition of polycardanol, PP and PP blend with 10% loading of

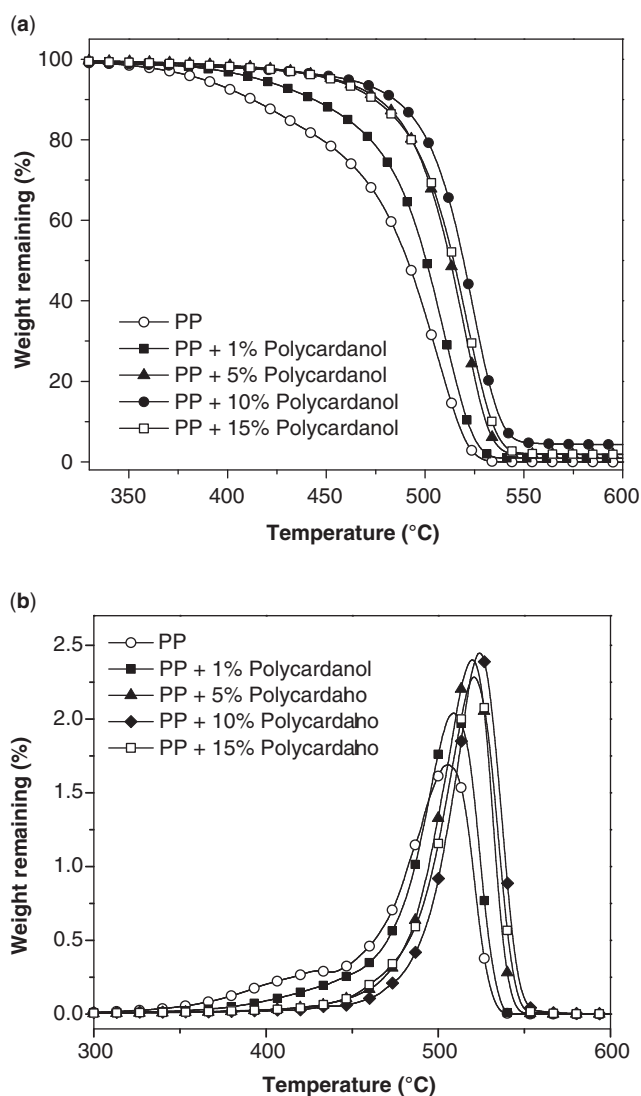


Figure 7 Thermogravimetric analysis curves for PP/Polycardanol blends: (a) TGA thermogram and (b) derivative-TGA thermogram.

polycardanol is plotted in Figure 8 (the IR absorption at specific wavenumbers are correlated to the gas species according to Singh *et al.* [47]). GRAMS/3D graphs were used to further explain the degradation pathway of the materials.

The peak height at a specific wavenumber represented the absorption of characteristic compounds or functional groups. The peak height as a function of time provided the evolution of specific compounds.

The degradation of polycardanol takes place in several stages. In the first stage, carbon dioxide was released from 6 mins (140°C) onwards. From 20 mins (420°C) onwards, alkanes and aromatics were released. In the second stage, volatile alkanes were released due to the degradation of the alkyl chains in cardanol. Aromatics were also released from the

degradation of polycardanol. The release of methane was mainly from the recombination of methyl radical and hydrogen radical. In the last stage, carbon monoxide was generated due to the decomposition of phenoxy radicals [48]. The remaining material was converted mainly to graphitic char. When comparing the Gram-Schmidt curves of polypropylene with polypropylene/polycardanol blends, the increased concentration of carbon dioxide and carbon monoxide in the blends were due to polycardanol. The PCFC test calculates the HRC based on the consumption of oxygen that oxidizes the volatiles in the combustor. The released carbon dioxide and char formation contribute to the low HRC result in the PCFC test.

In GRAMS/3D graph, the infrared spectra were arranged as a function of time. The evolution of gaseous species was clearly shown in Figure 9. A comparison of GRAMS/3D graph of PP with PP-10% polycardanol blends indicates that C-H peaks (around 2960 cm^{-1}) appear for a longer time scale (> 25 minutes) in the case of the blends. The release of carbon dioxide from these blends is possibly delayed due to the interaction between PP and polycardanol. Although the mechanism is not clearly understood, the evolution of carbon dioxide definitely contributes to the lowering of the heat release capacity of PP-polycardanol blends.

3.1.3 PCFC Studies of PP-Polycardanol Blends

Total heat release (THR): The THR for the sample is the area under the HRR versus temperature curve. The THR values in combination with char yields reveal the condensed phase action of the FR additive. Table 2 shows the summary of results from PCFC of PP/Polycardanol blends. It has been reported that phosphorous compounds when blended into PP at 10 weight % loading exhibit promising condensed phase action and intumescent behavior with close to 20% decrease in THR [49]. The use of polymeric FR additives based on polyhedral oligomeric silsesquioxanes (POSS), results in a 10% decrease in THR of PP blends at 10% FR loading [50]. With increasing addition of polycardanol in polypropylene, THR and HRC decrease accordingly (the THR in PP/1% polycardanol is higher than PP itself, possibly due to some low molecular weight impurity). The THR decreases about 7% with 15% loading of polycardanol. This is mainly due to the char-forming nature of polycardanol. It reduces the total amount of gaseous products during thermal decomposition. HRC of PP blends drops by about 23.4% with 15% loading of polycardanol.

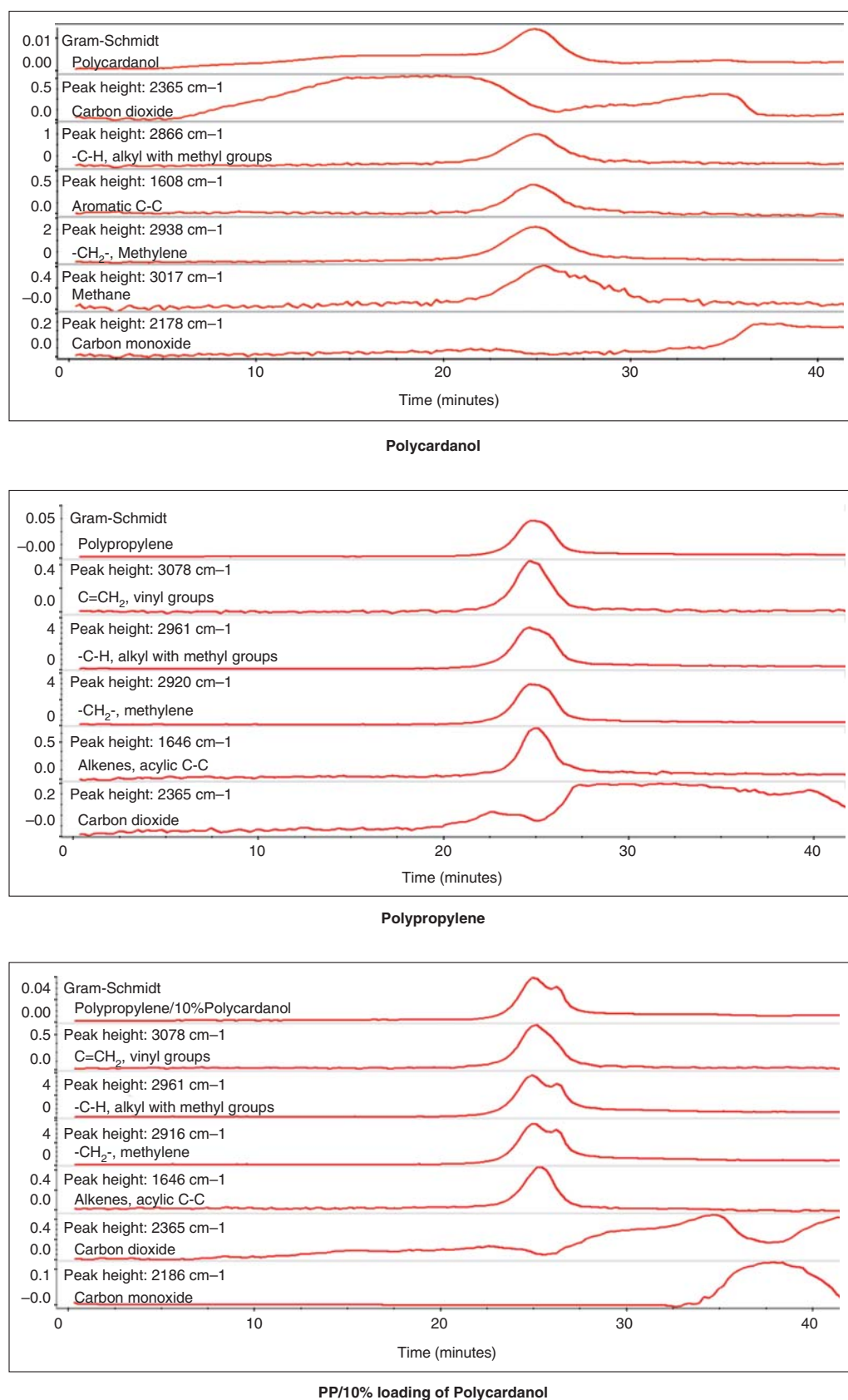
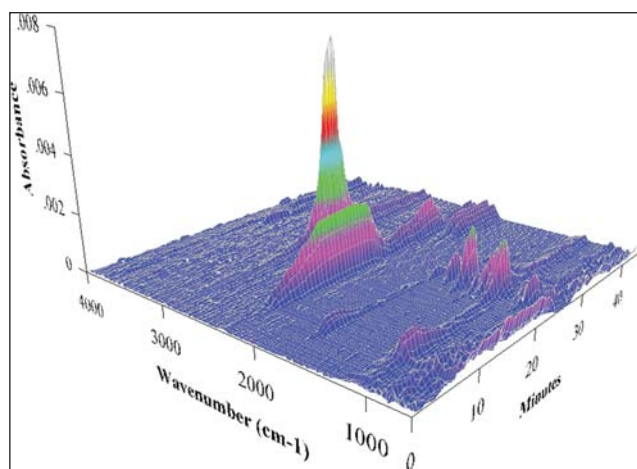
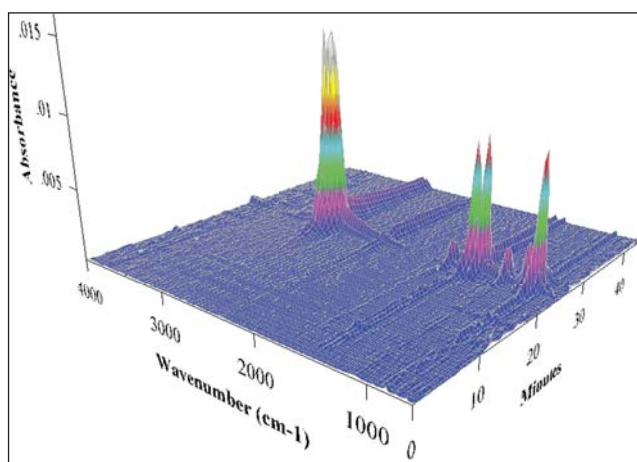


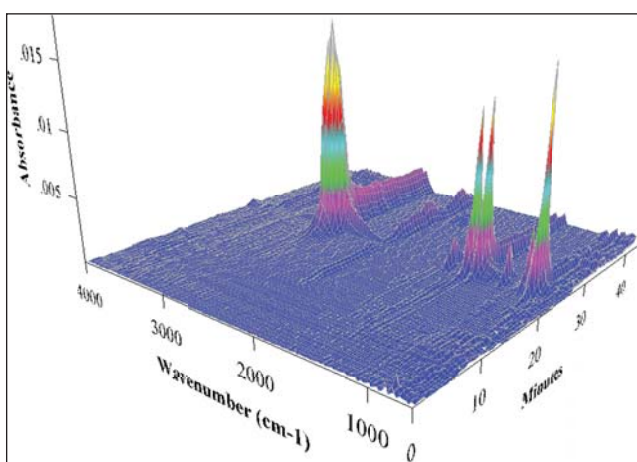
Figure 8 The evolution of gaseous products for PP, polycardanol and PP/10% loading of polycardanol.



Polycardanol



Polypropylene



Polypropylene/ 10% Polycardanol

Figure 9 GRAMS/3D graph of polycardanol, polypropylene and polypropylene/10% polycardanol.

Heat release rate: As shown in Figure 10(a), with increasing addition of polycardanol, the peak heat release rate (pHRR) of PP blends was lower. The temperature where the heat release peaks also shifts to a higher temperature (about 30°C), which is a good indicator of the improved thermal stability caused by the addition of polycardanol.

3.1.4 Comparison with Halogenated FR

With increasing amount of halogenated FR additives, PP shows a significant decrease in pHRR in PP/DBDPE blends (about 40%), and the HRR versus temperature curve are distributed over a larger range of temperatures (Figure 10(b)). The effect of the addition of HBCD to PP (as shown in Figure 10(c)) is similar to that of the addition of polycardanol to PP, as seen in the HRR vs temperature curve.

The comparison of HRC values of these blends is shown in Figures 10(d) and 11. One of the most efficient halogenated FR is DBDPE. There is a 50% reduction in HRC at 15% loading with respect to virgin PP. The HBCD is a moderate FR for bulk PP and fiber-grade PP and is often used in combination with metal hydroxide additive for synergistic action [51–53]. In our study, HBCD showed a 24% reduction in HRC at 15% loading. Polycardanol was as efficient as HBCD in the reduction of HRC (23% reduction) with 15% loading. The rate of oxygen consumption in the combustor is used to calculate HRC. Therefore HRC is closely related to the thermal decomposition rate and oxygen consumption during burning of degradation products. Although these results may not directly correlate with flammability tests, it is interesting to note that polycardanol shows promise in terms of improving the thermal stability of PP.

3.1.5 Rheological Studies

One of the major problems with inorganic FR additives is the change (increase of viscosity) of rheological properties at high filler loading. To be effective as FR, inorganic fillers have to be added at >25% by weight loading and the change of rheological properties do not permit this high level of loading in many applications. To explore if polycardanol adversely affects rheological properties of blends, the change of viscosity with shear rate was monitored in an ARES rheometer. Figure 12 illustrates the viscosity behavior of PP/polycardanol blends in a frequency sweep experiment done at 210°C. All curves present evidence of shear-thinning behavior with frequency indicating the pseudoplastic nature of the blends. The addition of polycardanol evidently increases viscosity, especially at lower frequencies. This is attributed to phase

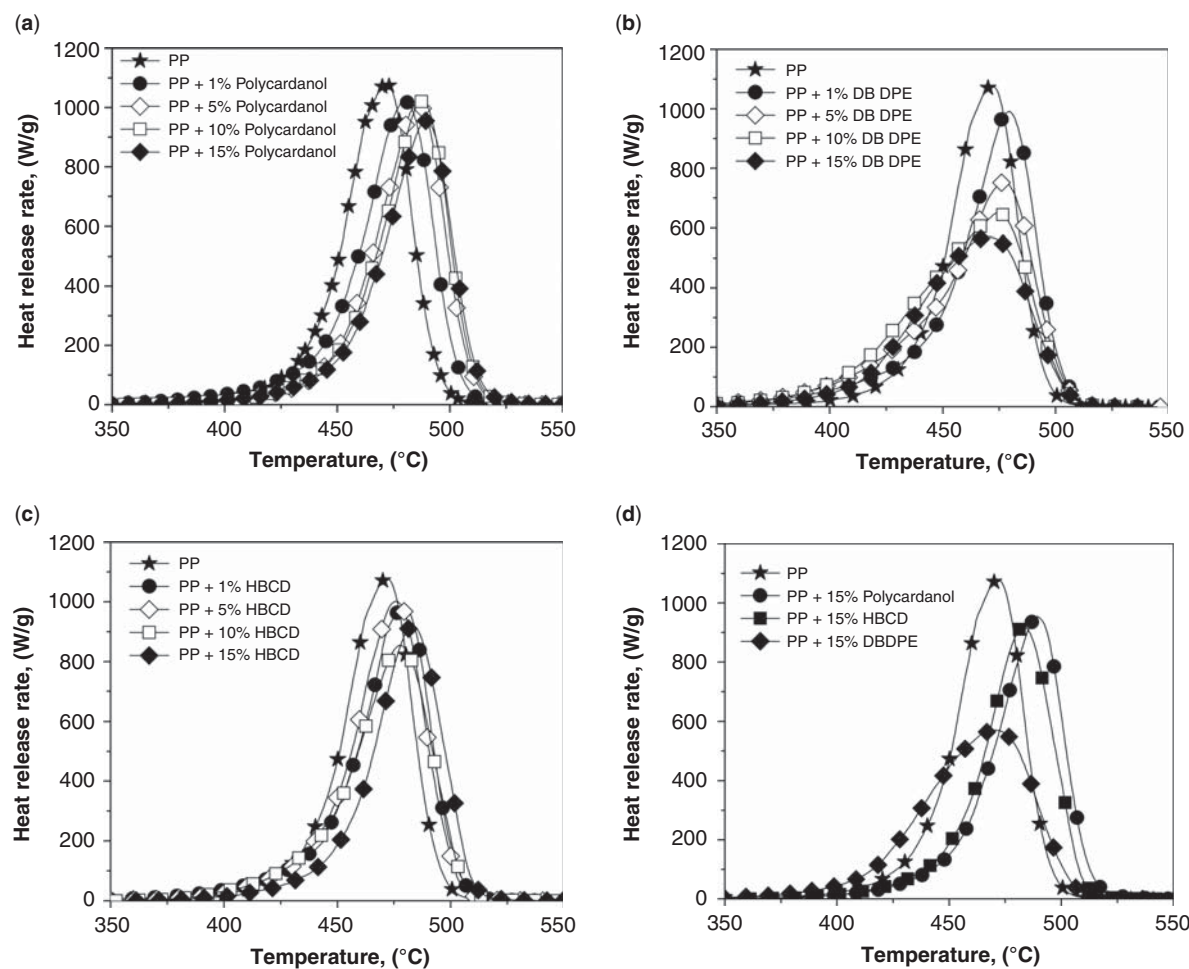


Figure 10 Heat release rate (HRR) versus temperature curves from PCFC test for (a) PP/Polycardanol, (b) PP/DBDPE, (c) PP/HBCD, and (d) comparison of polycardanol and halogenated FR.

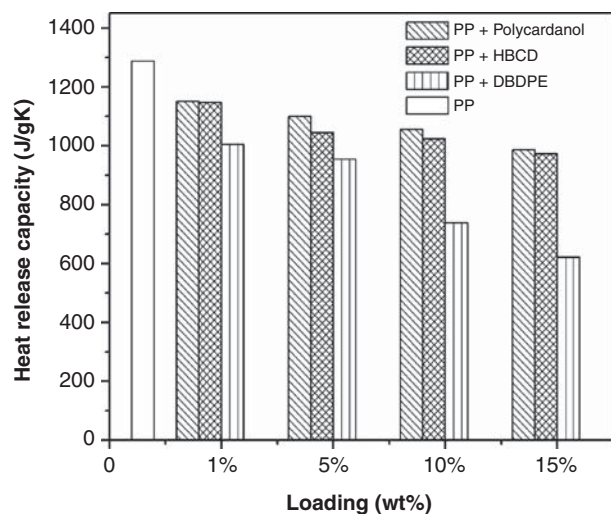


Figure 11 Comparison of HRC among PP/Polycardanol, PP/DBDPE and PP/HBCD blends.

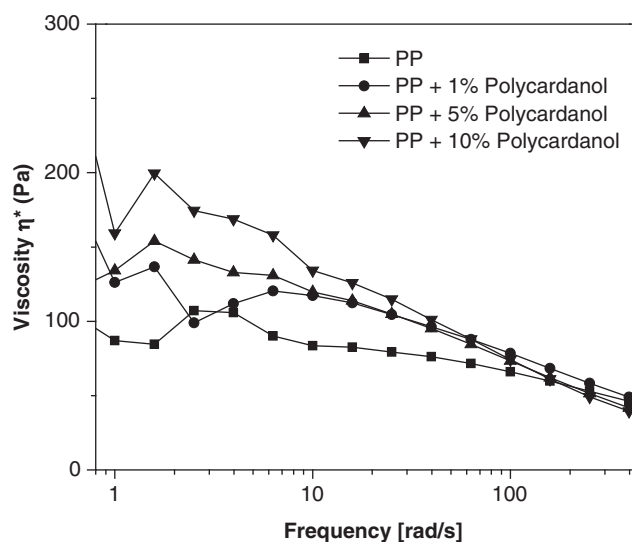


Figure 12 Viscosity vs shear rate curves in a frequency sweep experiment at 210°C for PP/polycardanol blends.

separation as previously observed for PP / novolac blends [54]. The difference in viscosities of PP/poly-cardanol (up to 10 wt% loading) in comparison to virgin resin is almost negligible at higher frequencies (shear rates most commonly used for injection molding and extrusion). It may therefore be concluded that polycardanol does not adversely affect the processing behavior of the blends.

3.2 Toxicity Studies

Polycardanol is being explored as a possible alternative to toxic halogenated FR. To ensure that polycardanol is not toxic, appropriate toxicity studies were carried out in accordance with the Organization for Economic Co-operation and Development (OECD) 425 guidelines for the testing of chemicals by Toxicon Inc. The results from this study indicate that LD₅₀ values for polycardanol is greater than 2000 mg/kg (more details of the test results are provided in the Supplementary Information S2).

4 CONCLUSION

This research has explored the possibility of using polymers derived from natural phenols as an alternative char-forming type FR. The low cost, bioderived cardanol could be polymerized to yield a polycardanol with improved thermal stability and reasonable compatibility with PP. Polycardanol could be easily dispersed into polyolefins such as PP and the blends, as they exhibited higher degradation temperatures, lower HRC and higher char yield. The performance of this polyphenol compares favorably with some commercially available halogenated FR purely from an HRC perspective. The TGA-FTIR evolved gas analysis studies indicate that the release of inert carbon dioxide and formation of char contributes to the lower HRC of polycardanol and PP-polycardanol blends. Polycardanol also seems to retard/delay the release of hydrocarbon-based degradation products from PP. The work presented in this research suggests that polyphenols have a place in the area of flame retardant materials. This opens new possibilities in the area of non-toxic fire resistant polymers based on polyphenols.

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