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Thiophosphate esters of cashew nutshell liquid derivatives as new antioxidants for poly(methyl methacrylate)

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Abstract In this work, poly(methyl methacrylate) films 1% additivated with new thiophosphate esters antioxidants derived from technical Cashew Nutshell Liquid (CNSL), a byproduct of the cashew nut (*Anacardium occidentale* L.) industry, were investigated by thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) measurements under inert (N_2) and oxidative (synthetic air) atmospheres. Three new products were synthesized and characterized by GC/MS, ^{1}H and ^{31}P NMR. The analyses were focused on the onset (T_e) and offset temperature (T_o) of degradation of the films, and on the maximum degradation temperature (T_{MAX}). It was observed that the thermal stability of the films increased with the addition of the thiophosphate ester antioxidants, which indicates that CNSL could be used as a natural source of phenolic material for the synthesis of antioxidants.

Keywords CNSL · Cardol · Cardanol · Thermogravimetry · DSC · PMMA

Introduction

Cashew nutshell liquid (CNSL), a byproduct of the cashew nut (*Anacardium occidentale* L.) processing in industry, is a replenishable oil, caustic, with a dark brownish color and a very characteristic odor.

Technical cashew nut shell liquid, name given to CNSL after the heat treatment to deshell the cashew industrially, is essentially a mixture of two phenolic lipids: cardanol and cardol (Fig. 1) both having degrees of saturation of the alkyl side chain varying from complete saturation to partial unsaturation (Fig. 1) [1, 2].

The global production of cashew nuts in 2008, according to the Food and Agriculture Organization of the United Nations (FAO), is around 3,700,000 million ton, and the greatest producers are Vietnam, India, Nigeria, Côte d'Ivoire, and Brazil, representing more than 80% of the total [3].

The main industrial applications of CNSL are in the form of brake linings, surface coatings, paints, varnishes, and polymers [4, 5].

The main component of technical CNSL, cardanol, comprising about 60–65% w/w, has been much studied, showing different applications: polymers [6], antioxidants [7], surfactants [8], flame-retardants [9], gum inhibitors for gasoline [10], and many others [11].

On the other hand, cardol, representing 15–20% w/w of the technical CNSL, is less studied than cardanol. Basically, the publications related to cardol concentrate in its biological activities, notably mollucisdal [12], larvicidal [13], antifilarial [14], and acetyl cholinesterase inhibitors [15].

As hindered phenols, cardanol and cardol could be employed as antioxidant, more specifically as primary type ones, i.e. preventing oxidative damage through the scavenging of free radicals, converting peroxy radicals to hydroperoxides by donation of their phenolic hydrogen atom [16].

Nevertheless, secondary types of antioxidants (also known as synergistic or preventive antioxidants) play as well an important role in preventing oxidation by reacting

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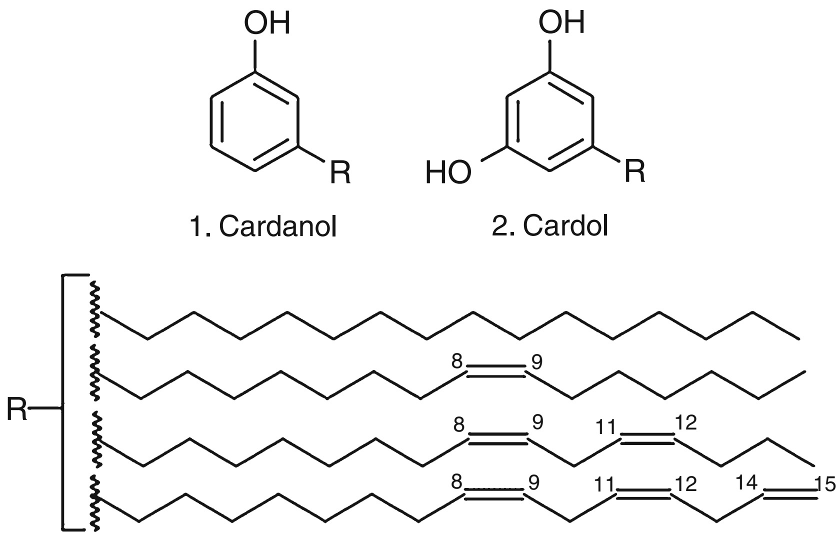

Fig. 1 The main components of technical CNSL: cardanol (1) and cardol (2)

with hydroperoxides formed by thermal oxidation reactions. In general, they are used in combination with primary antioxidants during processing and for long-time stabilization under severe thermal conditions. Among the substances used as secondary antioxidant, organophosphorus compounds are one of the most common, and thiophosphate esters are very useful substances that showed excellent activity as secondary antioxidants [17, 18].

In this way, the utilization of antioxidants of both types is very important in the prevention or retardation of degradation processes in different kinds of materials.

As for plastic materials, such as poly(methyl methacrylate), PMMA, the addition of antioxidants seems to be the most convenient way to retard oxidation acting as processing and long-term stabilizers. Although, it is also known that low molecular weight antioxidants can be easily removed from the polymer by volatilization, consequently the use of a higher mass component could reduce greatly this effect [19].

Poly(methyl methacrylate), is a transparent synthetic thermoplastic polymeric material, widely used in the industry, which shows great resistant to oxidative photodegradation [20], stability to sunlight [21], good weathering properties [22], and is also resistance to many inorganic reagents (including acidic or basic media), aliphatic hydrocarbons and non-polar solvents [23].

The main objectives of this work were to synthesize three thiophosphate esters from CNSL components, cardanol and cardol, characterize them by NMR ^{1}H and GC/MS and evaluate the thermal oxidative stability of PMMA films additivated with 1% of each of the prepared antioxidants using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC).

Experimental

Materials

The technical cashew nutshell liquid was supplied by Amêndoas do Brasil LTDA, a brazilian cashew company. All reagents and solvents were supplied by Sigma-Aldrich and Vetec Química. Column chromatography was run using silica gel 60 (70–230 mesh, Vetec Química), while TLC was conducted on precoated silica gel polyester sheets (Kieselgel 60 F254, 0.20 mm, Merck).

Measurements

The samples obtained were analyzed by GC–MS on a Hewlett–Packard Model 5971 using a (5%-phenyl)-methylpolysiloxane (DB-5) capillary column (30 m × 0.25 mm) with film thickness 0.1 mm; carrier gas helium, flow rate 1 mL min^{-1} with split mode. The injector temperature and detector temperature were 250 and 200 °C, respectively.

NMR spectra were recorded on a Bruker Avance DRX-300 (300 MHz for ^{1}H) using $CDCl_3$ as solvent.

Thermogravimetric measurements were carried out using a Mettler-Toledo TGA/SDTA851e thermogravimetric analyzer. Differential Scanning Calorimetry analyses were made using a Mettler-Toledo DSC 823e. All data obtained were analyzed using Mettler-Toledo STARe Software version 9.30. The measurements were performed at scanning rate of 10 °C min^{-1}, samples of approximately 5 mg were heated from 40 to 500 °C. The measurements were carried out in nitrogen (N_2) and/or synthetic air atmospheres (50 mL min^{-1}).

Isolation of cardol and cardanol

Cardanol (11.8 g) and cardol (2.1 g) were isolated from technical CNSL (20.0 g) using a silica gel column (Silica Gel 60) eluted with a stepwise gradient of *n*-hexane–ethyl acetate (from 9:1 to 7:3 by volume). The fractions obtained by this separation were analyzed through thin layer chromatography (TLC) and then reunited according their retention factors (RF).

Cardanol: light brownish oil, ^{1}H NMR (CDCl$_3$, δ): 1.03 (t, 3H); 1.45 (m); 2.19 (t, 2H); 5.13 (m); 5.21; 5.53 (m); 5.92 (m); 6.79 (m, 1H); 6.82 (m, 1H); 6.86 (s, 1H); 7.22 (t, 1H).

Cardol: dark brownish oil; ^{1}H NMR (acetone-D6, δ): 0.80 (t, 3H); 1.26 (m); 1.51 (m); 2.05 (m); 2.39 (t); 2.75 (m); 4.94 (m); 5.31 (m); 5.77 (m); 6.05 (t, 1H); 6.09 (d, 2H).

Syntheses of thiophosphate esters of CNSL derivatives

The syntheses scheme of the thiophosphate antioxidants is shown in Fig. 2.

Synthesis of Cdn-detp (**3**)

To a solution of cardanol (**1**) (1,000 mg, 3.31 mmol) and potassium carbonate (456.7 mg, 3.31 mmol) in chloroform (60 mL), diethyl chlorothiophosphate (624.3 mg, 0.52 mL, 3.31 mmol) was added at room temperature. The resulting mixture was warmed to reflux temperature (60 °C) and stirred for 4 h. Brine (40 mL) was added, and the resultant solution was extracted with ethyl acetate (40 mL × 3). The combined organic extracts were dried over anhydrous NaSO$_4$, and concentrated in vacuum. The crude product was then purified by column chromatography using hexane–ethylacetate (9:1) as the eluant, to afford **3** (1,172 mg, 78%) as a yellow oil: ^{1}H NMR (300 MHz, CDCl$_3$) 0.91, m, R–CH_3; 1.26–1.43, m, –CH_2–CH_2– and P–O–CH$_2$–CH_3; 1.6, m, –CH_2–CH$_2$–Ar; 2.02, m, –CH=CH–CH_2–; 2.59, t, –CH_2–Ar; 4.23, m, –CH_2–O–P; 5.32, m, –CH=CH–; 6.99, s, Ar–*H* (*o*- and *p*-); 7.22, t, Ar–*H* (*m*-). ^{31}P NMR (121 MHz, CDCl$_3$) 64.2. GC/MS *m*/*z* (M$^+$): 454.

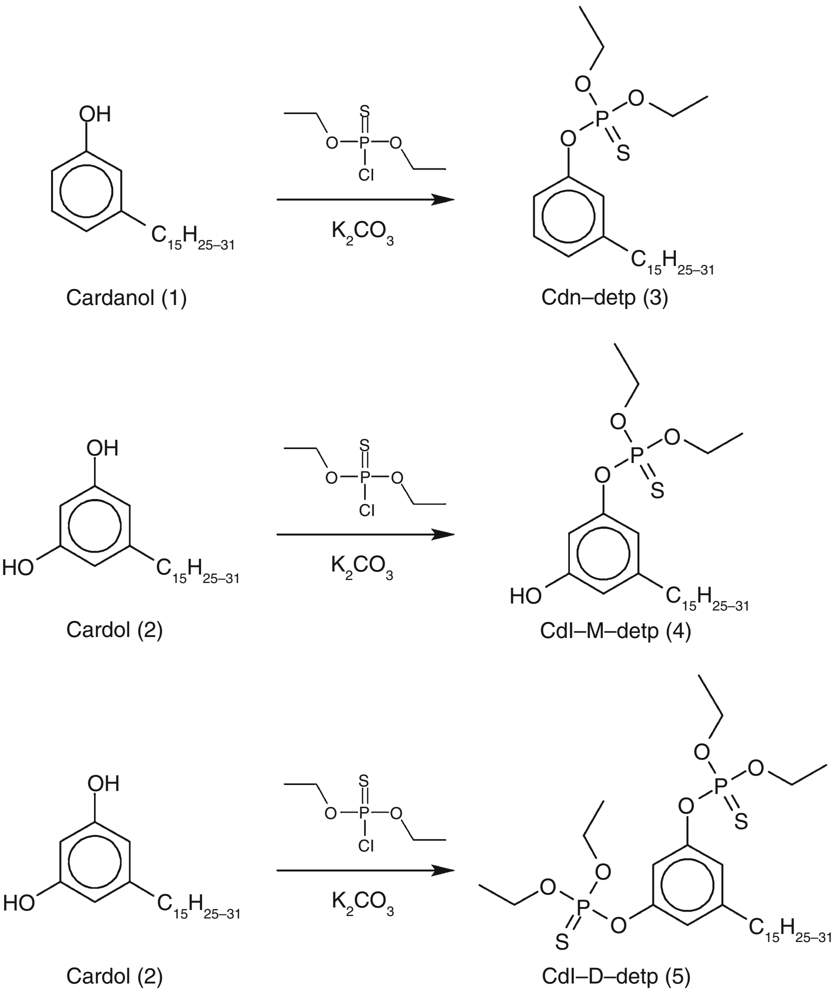

Fig. 2 Scheme of the syntheses of the thiophosphate esters of cardanol (1) and cardol (2)

Synthesis of Cdl-M-detp (4)

To a solution of cardol (**2**) (1,000 mg, 3.18 mmol) and potassium carbonate (438.84 mg, 3.18 mmol) in chloroform (60 mL), diethyl chlorothiophosphate (600.6 mg, 0.50 mL, 3.18 mmol) was added at room temperature. The resulting mixture was warmed to reflux temperature (60 °C) and stirred for 4 h. Brine (40 mL) was added, and the resultant solution was extracted with ethyl acetate (40 mL × 3). The combined organic extracts were dried over anhydrous $NaSO_4$, and concentrated in vacuum. The crude product was then purified by column chromatography using hexane–ethylacetate (7:3) as the eluant, to afford **4** (1,054 mg, 71%) as a dark yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) 0.91, t, R–CH_3; 1.26, t, P–O–CH_2–CH_3; 1.31–1.38, m, –CH_2–CH_2–; 1.57–1.59, m, –CH_2–CH_2–Ar; 2.03–2.07, m, –CH=CH–CH_2–; 2.58, t, –CH_2–Ar; 4.18–4.28, m, –CH_2–O–P; 4.96–5.08, m, –CH=CH_2; 5.33–5.45, m, –CH=CH–; 5.77–5.86, m, –CH=CH_2; 6.85, s, Ar–H (2 H); 6.91, d, Ar–H (1 H). ^{31}P NMR (121 MHz, $CDCl_3$) 64.6. GC/MS *m*/*z* (M^+): 468 and 466.

Synthesis of Cdl-D-detp (5)

To a solution of cardol (**2**) (1,000 mg, 3.18 mmol) and potassium carbonate (877.68 mg, 6.36 mmol) in chloroform (80 mL), diethyl chlorothiophosphate (1,201 mg, 1 mL, 6.36 mmol) was added at room temperature. The resulting mixture was warmed to reflux temperature (60 °C) and stirred for 8 h. Brine (40 mL) was added, and the resultant solution was extracted with ethyl acetate (40 mL × 3). The combined organic extracts were dried over anhydrous $NaSO_4$, and concentrated in vacuum. The crude product was then purified by column chromatography using hexane–ethylacetate (9:1) as the eluant, to afford **4** (1,003 mg, 51%) as a dark yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) 0.90, t, R–CH_3; 1.25, t, P–O–CH_2–CH_3; 1.32–1.38, m, –CH_2–CH_2–; 1.56–1.58, m, –CH_2–CH_2–Ar; 2.00–2.05, m, –CH=CH–CH_2–; 2.57, t, –CH_2–Ar; 4.17–4.29, m, –CH_2–O–P; 4.95–5.01, m, –CH=CH_2; 5.32–5.43, m, –CH=CH–; 5.75–5.87, m, –CH=CH_2; 6.84, s, Ar–H (2 H); 6.91, s, Ar–H (1 H). ^{31}P NMR (121 MHz, $CDCl_3$) 62.1. GC/MS *m*/*z* (M^+): 618 and 620.

Preparation of PMMA films

Films of PMMA, with and without additives, were prepared as described previously on literature [18], with few procedural modifications, by a solvent casting technique. The exact amount of each antioxidant, 1%, was added to a solution of 10% PMMA in dichloromethane which was gently homogenized by magnetic stirring. The blended samples were poured onto glass plates (Petri dish) and let to dry for 24 h at room temperature (28 °C).

Results and discussion

Thermogravimetric analyses (TG)

The thermal decomposition behavior of the PMMA films was studied through TG, under two different atmospheres: inert (N_2) and oxidative (air). Figure 3 shows the TG curves of PMMA pure and additivated with 1% of Cdn-detp, Cdl-M-detp, and Cdl-D-detp under N_2.

Figure 4 shows the DTG of the thermogravimetric analyses of PMMA pure and additivated with 1% of Cdn-detp, Cdl-M-detp, and Cdl-D-detp under N_2.

In the thermogram of PMMA showed in Fig. 3, it is possible to observe the presence of two distinct processes of mass loss. These two processes are explained by the mechanism of degradation of PMMA (Fig. 5). Previous studies, with the use of various oligomers as model compounds, reported that the least stable linkage in the oligomers was the H–H linkage (Fig. 5a) [24]. While the second event appears to be caused by random scission initiation (b), as shown in Fig. 5.

The determined onset (T_e), offset (T_o), and maximum degradation (T_{MAX}) temperatures for the TG curves of PMMA films shown in Figs. 3 and 4 are summarized in Table 1.

By the thermogravimetric results, the addition of the thiophosphate esters increased both the onset (T_e) and offset (T_o) temperatures of PMMA films. The presence of the phosphate group was of great importance in retarding the beginning of the oxidation process, as can be seen in the Cdn-detp (**3**) and Cdl-D-detp (**5**) additivated sample

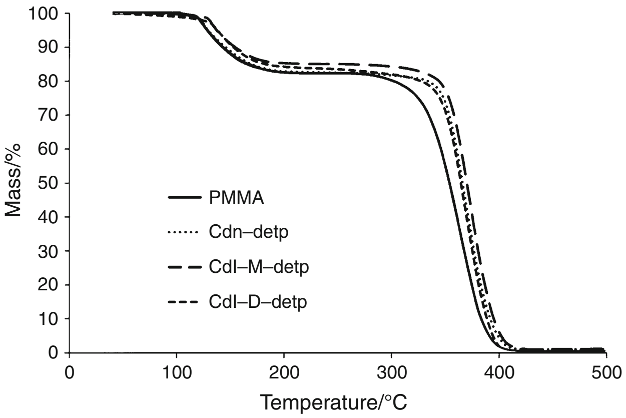

Fig. 3 Thermogravimetric analyses of PMMA films 1% additivated under N_2

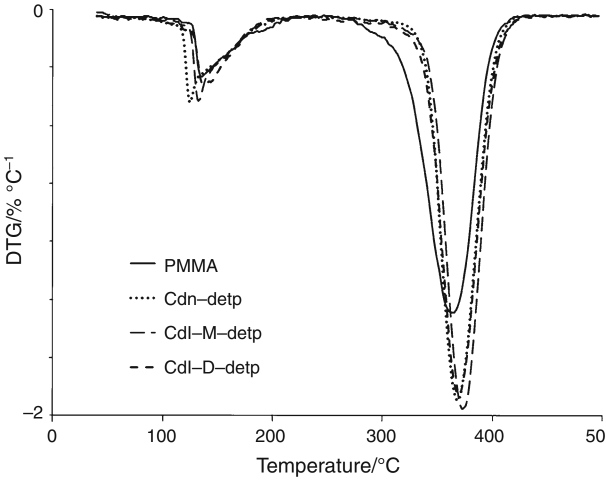

Fig. 4 DTG analyses of PMMA films 1% additivated under N_2

curves. However, the activity presented by the *hybrid* antioxidant Cdl-M-detp (**4**) was much better than that showed by the others compounds. Notably, the presence of the hydroxyl and thiophosphate groups, i.e. primary and secondary types of antioxidant, together in the same molecule was responsible for an increase of more than 10 °C in the T_e and T_{MAX} of the PMMA film sample.

In order to evaluate the behavior of PMMA films in environmental conditions, we also analyzed through thermogravimetry under oxidative atmosphere (synthetic air) the additivated samples. Figure 6 shows the TG curves for the PMMA films analyses.

Figure 7 shows the DTG of the thermogravimetric analyses of PMMA pure and additivated with 1% of Cdn-detp, Cdl-M-detp, and Cdl-D-detp under air.

In Table 2 are summarized the determined onset (T_e), offset (T_o), and maximum (T_{MAX}) degradation temperatures of the analyzed samples, showed in Figs. 6 and 7.

The antioxidant activities demonstrated by the thiophosphate esters of CNSL under oxidative atmosphere were slightly better than that under nitrogen atmosphere. Once again, the *hybrid* antioxidant Cdl-M-detp showed an excellent activity, increasing in 18 °C the onset temperature (T_e), and 35 °C in both the offset (T_o) and the maximum degradation temperatures (T_{MAX}).

Table 1 Temperatures determined for the TG analyses of PMMA film samples under inert atmosphere

Samples	Temperatures/°C		
	T_e	T_o	T_{MAX}
PMMA	343.74	386.55	368.43
+1% Cdn-detp	349.32	390.37	369.83
+1% Cdl-M-detp	352.31	393.59	375.17
+1% Cdl-D-detp	348.23	390.09	370.83

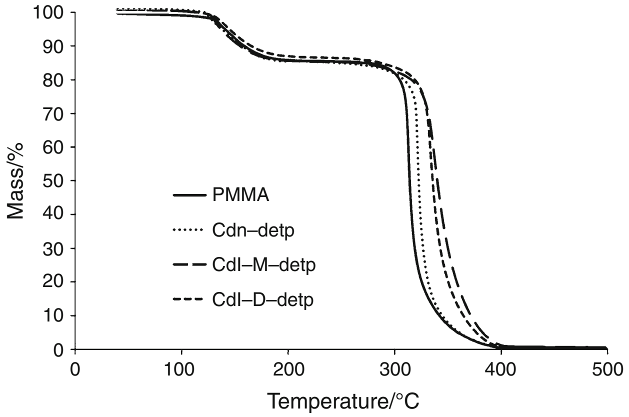

Fig. 6 Thermogravimetric analyses of PMMA films 1% additivated under air

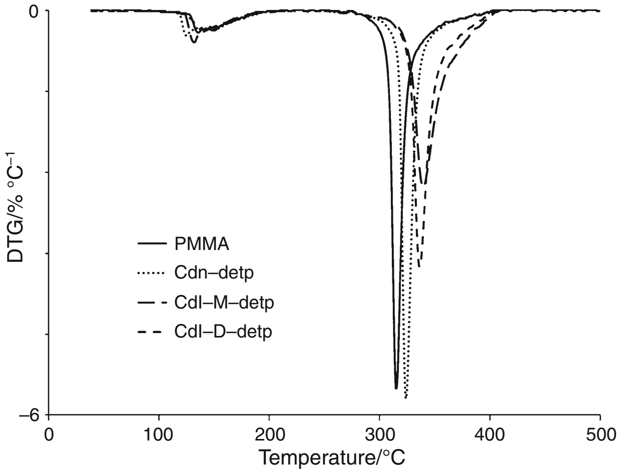

Fig. 7 DTG analyses of PMMA films 1% additivated under air

Fig. 5 Mechanisms of two different PMMA degradation processes

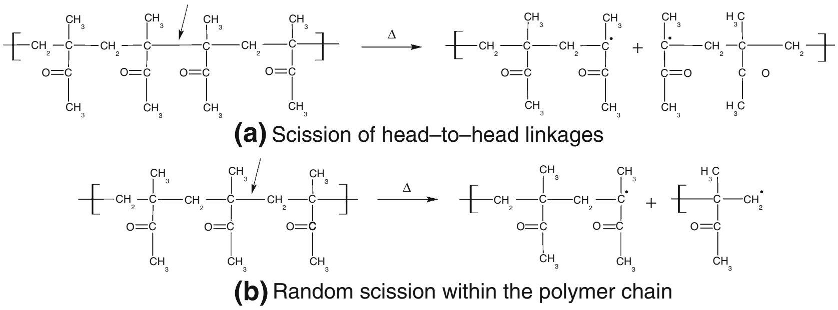

Table 2 Temperatures determined for the TG analyses of PMMA film samples under air atmosphere

Samples	Temperatures/°C		
	T_e	T_o	T_{MAX}
PMMA	310.18	322.89	315.83
+1% Cdn-detp	318.81	331.30	324.67
+1% Cdl-M-detp	328.27	358.78	340.00
+1% Cdl-D-detp	327.16	349.04	337.00

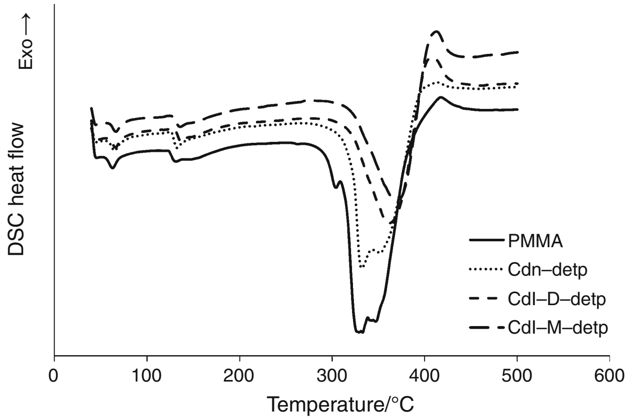

Fig. 8 DSC analyses of PMMA films 1% additivated under N_2

Table 3 Temperatures determined for DSC analyses of PMMA film samples under N_2 atmosphere and for the mass loss of 30, 50, and 70%

Samples	Thermal degradation onset temperature/°C	Total mass loss % at °C		
		30%	50%	70%
PMMA pure	291.37	337.57	354.98	367.72
+1% Cdn-detp	315.48	351.89	364.17	374.95
+1% Cdl-M-detp	318.09	355.93	368.08	379.02
+1% Cdl-D-detp	314.76	349.24	363.18	373.78

Cdl-D-detp also presented very good results, demonstrating that the thiophosphate group itself can promote an antioxidant effect similar to that showed by Cdl-M-detp, retarding the beginning of degradation by the increase of onset temperature, though the effect on offset temperature is still lower than of the hybrid compound, which can indicate a better effect promoted by the hydroxyl group.

Differential scanning calorimetry (DSC) analyses

The thermal degradation onset temperature measured by differential scanning calorimetry is observed as the point at which the slope of the DSC endotherm curve increases sharply.

Figure 8 shows the DSC analyses curves for the additivated PMMA films under a N_2 atmosphere.

Table 3 summarizes thermal degradation onset temperatures and percent mass loss data of PMMA films additivated with thiophosphate esters of CNSL. These data are based on DSC and TG measurements under nitrogen atmosphere.

From the data presented in Table 3, it is apparent that Cdl-M-detp (**4**) increased thermal stability of PMMA films in comparison to Cdn-detp and Cdl-D-detp. Once again, the enhanced stability of Cdl-M-detp can be related to its basic structure (Figs. 2, 4) which posses both hydroxyl and thiophosphate groups, primary and secondary types of antioxidants.

Conclusions

In summary, three thiophosphate esters of technical CNSL components, cardanol and cardol, were prepared, and their structure confirmed by GC/MS, ^{1}H, and ^{31}P NMR analyses. To evaluate the antioxidant capacity of Cdn-detp, Cdl-M-detp, and Cdl-D-detp on the thermo-oxidative stability of 1% additivated PMMA films, differential scanning calorimetry (DSC) and thermogravimetry analyses (TG) were used. By the TG analyses, the values of onset (T_e), offset (T_o), and maximum degradation (T_{MAX}) temperatures were increased with the additivation of PMMA films with each of the components in both inert and oxidative atmospheres. The DSC analyses under nitrogen confirmed that Cdl-M-detp was the best antioxidant with an increase in the onset temperature (T_e) of degradation of PMMA in more than 10%. The thermogravimetry results showed an increased in almost 6% the value of the onset temperature (T_e) and more than 15% the offset temperature (T_o), the maximum degradation temperature (T_{MAX}) increased up to 8%. This was probably due to its hybrid structure, which owns both hydroxyl group, responsible for primary antioxidant behavior, and thiophosphate group, responsible for the secondary antioxidant behavior. In this sense, the utilization of technical CNSL as raw material in the synthesis of new products is a good natural alternative to petrochemical-derived phenol, a product whose price is inherently linked to the unstable oil price and availability of fossil fuels.

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References

1. Mazzetto SE, Lomonaco D, Mele G. Cashew nut oil: opportunities and challenges in the context of sustainable industrial development. Quim Nova. 2009;32:732–41.
2. Sousa Rios MA, Santiago SN, Lopes AAS, Mazzetto SE. Antioxidative activity of 5-n-pentadecyl-2-tert-butylphenol stabilizers in mineral lubricant oil. Energy Fuels. 2010; 24:3285–91.
3. Food and Agriculture Organization of United Nation. In: FAOSTAT, 2010. http://faostat.fao.org/site/339/default.aspx. Accessed 01 Oct 2010.
4. Talbiersky J, Polaczek J, Ramamoorty R, Shishlov O. Renewables: phenols from cashew nut shell oil as a feedstock for making resins and chemicals. Oil Gas Eur Mag. 2009;35:33–9.
5. Paramashivappa R, Phani Kumar P, Vithayathil PJ, Srinivasa Rao A. Novel method for isolation of major phenolic constituents from cashew (*Anacardium occidentale* L.) Nut shell liquid. J Agri Food Chem. 2001;49:2548–51.
6. Yadav R, Srivastava D. The effect of CTBN concentrations on the kinetic parameters of decomposition of blends of cardanol-based epoxidized novolac resin modified with carboxyl-terminated liquid copolymer. J Appl Polym Sci. 2009;114:1694–701.
7. Trevisan MT, Pfundstein B, Haubner R, Wurtele G, Spiegelhalder B, Bartsch H, Owen RW. Characterization of alkyl phenols in cashew (*Anacardium occidentale*) products and assay of their antioxidant capacity. Food Chem Toxicol. 2006;44:188–97.
8. Peungjitton P, Sangvanich P, Pornpakakul S, Petsom A, Roengsumran S. Sodium cardanol sulfonate surfactant from cashew nut shell liquid. J Surfactants Deterg. 2009;12:85–9.
9. Ravichandrana S, Bouldinb RM, Kumarc J, Nagarajan R. A renewable waste material for the synthesis of a novel non-halogenated flame retardant polymer. J Clean Prod. 2010. doi: 10.1016/j.jclepro.2010.09.010.
10. Castro Dantas TN, Dantas MSG, Dantas Neto AA, D'Ornellas CV, Queiroz LR. Novel antioxidants from cashew nut shell liquid applied to gasoline stabilization. Fuel. 2003;82:1465–9.
11. Mele G, Vasapollo G. Fine chemicals and new hybrids materials from cardanol. Mini Rev Org Chem. 2008;5:243–53.
12. Stasiuk M, Kozubek A. Biological activity of phenolic lipids. Cell Mol Life Sci. 2010;67:841–60.
13. Lomonaco D, Santiago GMP, Ferreira YS, Arriaga AMC, Mazzetto SE, Mele G, Vasapollo G. Study of technical CNSL and its main components as new green larvicides. Green Chem. 2009; 11:31–3.
14. Suresh M, Kaleysa Raj R. Cardol: the antifilarial principle from *Anacardium occidentale*. Curr Sci. 1990;59:477–9.
15. Stasiuk M, Bartosiewicz D, Kozubek A. Inhibitory effect of some natural and semisynthetic phenolic lipids upon acetylcholinesterase activity. Food Chem. 2008;108:996–1001.
16. Klein E, Lukes V, Cibulkova Z. On the energetics of phenol antioxidants activity. Petrol Coal. 2005;47:33–9.
17. Pèrez-Lamela C, Rijk R, Simal-Gándara J. Stability of the secondary antioxidant bis(2,4-di-tert-butylphenyl)pentaerythritol. Diphosphite Food Simulants. 1998;46:687–91.
18. De Sousa Rios MA, Nascimento TL, Santiago SN, Mazzetto SE. Cashew nut shell liquid: a versatile raw material utilized for syntheses of phosphorus compounds. Energy Fuels. 2009;23:5432–7.
19. Chang TC, Yua PY, Honga YS, Wub TR, Chiu YS. Effect of phenol phosphate antioxidant on the thermo-oxidative degradation of PMMA. Polym Degrad Stab. 2002;77:29–34.
20. Hawkins WL. Polymer stabilisation. New York: Wiley Interscience; 1972.
21. Bamfor CH, Tipper CFH. Degradation of polymers. Amsterdam: Elsevier; 1975.
22. Billmeyer FW. Textbook of polymer science. 3rd ed. New York: Wiley; 1984.
23. Gross S, Camozzo D, Di Noto V, Armelao L, Tondello E. PMMA: a key macromolecular component for dielectric low-[kappa] hybrid inorganic-organic polymer films. Eur Polym J. 2007;43:673–96.
24. Kashiwagi T, Inaba A, Brown JE, Hatada K, Kitayama T, Masuda E. Effects of weak linkages on the thermal and oxidative degradation of poly(methyl methacrylates). Macromolecules. 1986;19:2160–8.