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MODIFICATION OF NATURAL RUBBER WITH PHOSPHATIC PLASTICIZERS: A COMPARISON OF PHOSPHORYLATED CASHEW NUT SHELL LIQUID PREPOLYMER WITH 2-ETHYL HEXYL DIPHENYL PHOSPHATE

A. R. R. MENON,[1] C. K. S. PILLAI[1]* and G. B. NANDO[2]

[1]Regional Research Laboratory (CSIR), Thiruvananthapuram 695 019, India and [2]Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302 (WB), India

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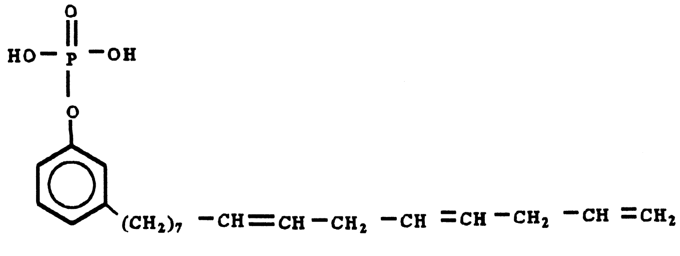
Abstract—The vulcanization characteristics, tensile properties, thermal decomposition characteristics and flame retardancy of Natural Rubber (NR) modified with phosphorylated cashew nut shell liquid (PCNSL) prepolymer has been studied and compared with 2-ethyl hexyl diphenyl phosphate (Santicizer-141), at concentrations ranging from 10 to 20 phr. The PCNSL modified NR vulcanizates showed higher tensile properties and resistances to thermo-oxidative decomposition and flame compared to that containing similar dosages of Santicizer. Kinetic parameters for themo-oxidative decomposition, obtained from dynamic thermogravimetry, indicated a higher degree of condensed phase reactions for the PCNSL modified NR vulcanizates, especially at higher heating rates and in presence of higher concentrations of PCNSL. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Physical modification of polymers with plasticizers has long been practised as a means to improve the processability of the compounds and the physico-mechanical properties of the final products. However, in many of the specialized applications flame retardancy has taken the priority as an essential service requirement. Therefore, the plasticizer to be used should invariably have flame retardant nature. In this respect, phospatic plasticizers holds a place of great significance [1]. This is evident from a wide variety of such plasticizers being used for modification of plastics and elastomers [2]. One of the essential aspects to be looked at, while using such plasticizers, is that along with improved processability, they should not affect the physico-mechanical properties of the final product adversely. An attempt to improve the flame retardancy of epoxidized liquid natural rubber by modification with dibutyl phosphate resulted in a decrease in the rate of cure and mechanical properties [3]. We have observed considerable improvements in the processability characteristics [4, 5] and physico-mechanical properties [6, 7] of natural rubber (NR) modified with 5 to 20 phr of phosphorylated cashew nut shell liquid (PCNSL) prepolymer. PCNSL (I) is an oligomeric flame retardant plasticizer compatible with a variety of plastics and elastomers.



(I) Structure of the triene component of phosphorylated cardanol, the major constituent of PCNSL

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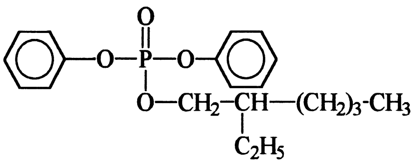
*To whom all correspondence should be addressed.

The advantage of oligomeric flame retardants [8] over the low molecular weight counter-parts with respect to permanence/durability in service is well known. They have low volatility, lower decomposition temperatures, lower viscosity and combine more readily with the polymer base [9]. The possibility for presence of highly toxic impurities in commercial grades of flame retardant plasticizers such as tri cresyl phosphate (TCP) and tri xylyl phosphate (TXP) limits their wide-spread use [10]. Other phosphatic plasticizers such as 2-ethyl hexyl diphenyl phosphate and isodecyl diphenyl phosphate are reported to offer a compromise between flame retardancy and low temperature properties in rubber products [11]. 2-Ethyl hexyl diphenyl phosphate (Santicizer 141) (II) [12] has been shown to be an ideal non-toxic flame retardant plasticizer for poly vinyl chloride [13] and nitrile rubber [14].



(II). 2-ethyl hexyl diphenyl phosphate

We report in this paper, the results of a comparative study carried out with 10 to 20 phr each of PCNSL and Santicizer 141 in a typical semi efficient vulcanization (SEV) system of NR — highlighting the vulcanization characteristics and physicomechanical properties of the vulcanizates such as tensile properties along with properties such as flame resistance and resistance to thermo-oxidative decomposition of the vulcanizates.

EXPERIMENTAL

Cashew nut shell liquid (CNSL) conforming to Indian Standard (IS:840(1964)) was obtained from M/s Vijayalakshmi Cashew Factory, Kollam. PCNSL was synthesized by phosphorylating pre-heated CNSL with *o*-phosphoric acid at 175 ± 5°C for 4 h by a patented process [15].

2-Ethyl hexyl diphenyl phosphate (Santicizer 141) was obtained from Monsanto Chemical, U.S.A. Indian standard natural rubber (ISNR-5) was obtained from the Rubber Research Institute of India. Other chemicals such as zinc oxide, stearic acid, sulphur, mercapto benzo thiazole sulphenamide (MBT) and tetra methyl thiuram disulphide (TMTD) were of the laboratory reagent grade.

NR formulations as given in Table 1 were mixed on a two roll mixing mill (size 150 × 300 mm) at a friction ratio of 1:1.12. Vulcanization characteristics of the formulations at 150°C were measured on an oscillating disk rheometer (Monsanto, R-100) as per ASTM D-2084-81. Test specimens were moulded on an electrically heated hydraulic press at 150°C at the optimum cure times as determined above. Tensile properties of the vulcanizates were measured on a Zwick tensile tester (Model 1435) at a crosshead speed of 500 mm/min as per ASTM D-412-87 (Method-A). Accelerated ageing of the test specimens was carried out in a hot air oven, at 70°C for 12 h, as per ASTM D-573-78. Thermal decomposition characteristics of the specimens in air at the temperature range from 30 to 700°C were measured on a thermogravimetric analyzer (DuPont 951) coupled to a data processor (Thermal Analyst-2000) at the heating rates of 10, 20 and 40°C/min. Activation energy for decomposition at the temperature range from 310 to 360°C was calculated by the method of Freeman and Carroll [16]. The flame retardancy of the vulcanizates as given by limiting oxgen index (LOI) was measured on an oxygen index tester (Stanton-Redcroft-FTA) as per ASTM D-2863-77.

RESULTS AND DISCUSSION

Vulcanization characteristics

The rheographs of the samples cured at 150°C are shown in Fig. 1. The cure parameters such as scorch time, optimum cure time, and cure rate of the mixes are given in Table 2. Table 2 indicates greater scorch safety for the mixes modified with PCNSL as compared to those containing Santicizer. This behaviour is observed only at higher concentrations of PCNSL such as 15 and 20 phr. However, the cure rates of the PCNSL modified stocks were much lower than that of those containing the same concentration of Santicizer and even lower than that of the reference sample. This is reflected in the relatively higher optimum cure times of the PCNSL modified mixes (P_{15} and P_{20}). Also, an increase in concentration of the plasticizer from 10 to 20 phr resulted in a drastic reduction in the maximum state of cure for the PCNSL modified mixes compared to that for the mixes containing Santicizer. This is significant, as higher doses of PCNSL reduces the crosslinking efficiency as reported earlier by the authors [6], due to the blockage of the activation effect of ZnO at normal dosage. An increase in ZnO dosage to the extent of 1:1 of ZnO and PCNSL, however, enhances the cure efficiency. This has been confirmed from the chemical analysis of these vulcanizates [17]. The reductions in chemical crosslink density at higher concentrations of PCNSL and at lower doses of ZnO were supposed to be due to complex-formation between the phosphate group of PCNSL and ZnO leading subsequently to cure retardation [17]. The

Table 1. Composition of the mixes (phr)

Mix code	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}	U
NR	100	100	100	100	100	100	100
ZnO	10	10	10	10	10	10	10
Stearic acid	2	2	2	2	2	2	2
Sulphur	2	2	2	2	2	2	2
MBT	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PCNSL	10	15	20	–	–	–	–
Santicizer141	–	–	–	10	15	20	–

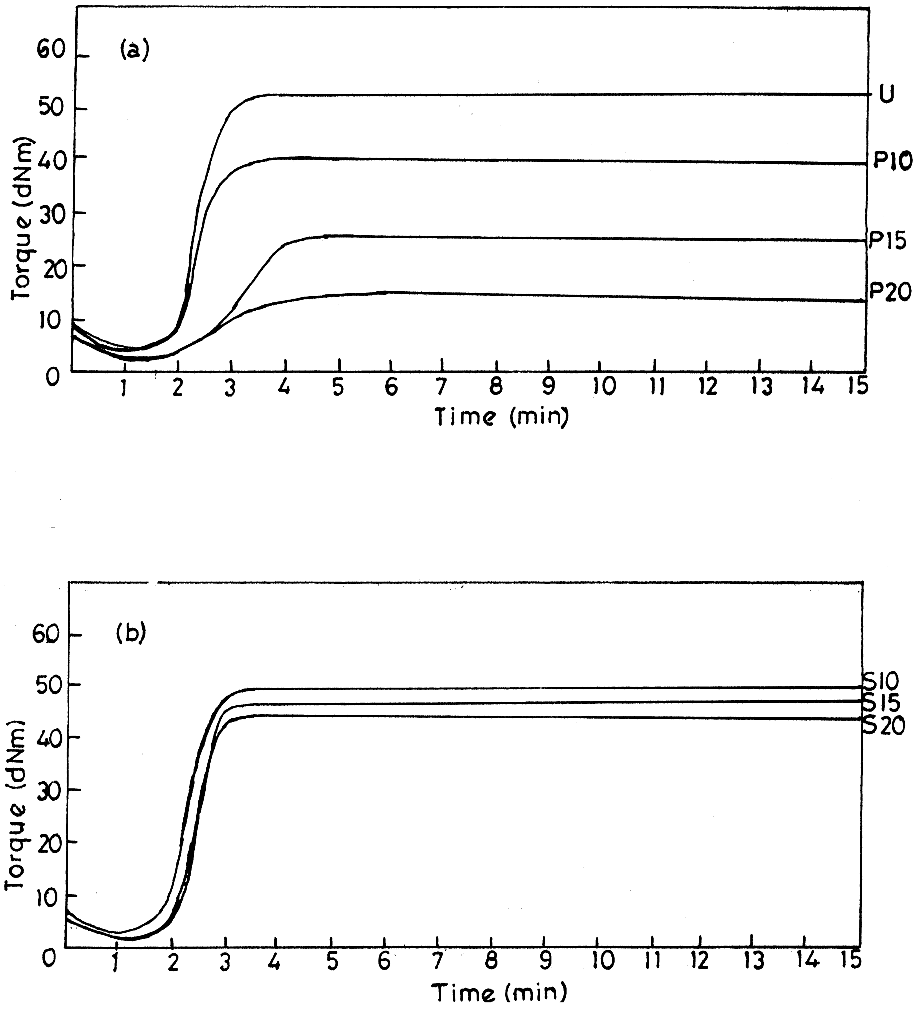


Fig. 1. Rheographs of the formulations at 150°C: (a) unmodified and PCNSL modified, and (b) Santicizer modified.

relatively higher rate and state of cure of the Santicizer-modified formulations (even at the higher concentration of 15 and 20 phr) indicates higher degrees of crosslinking, possibly due to the lack of interactions (e.g., H-bonding) between the phosphate group of Santicizer and ZnO, as mentioned above. This may be due to the presence of two bulky phenyl groups at the phosphate moeity, debarring the oxygen atoms to take part in H-bond formation.

Physico-mechanical properties compatibility

Modification of NR with PCNSL resulted in comparatively softer vulcanizates with lower stiffness and greater flexibility. The dispersion of the plasticizer in the NR matrix was very good indicating a higher degree of compatibility. However, the Santicizer modified vulcanizates showed an undesirable surface-bloom (especially at the higher concentrations of the plasticizer), possibly due to the poor compatibility with the NR matrix. From the above, it seems that PCNSL acts as a primary plasticizer in NR and Santicizer as a secondary plasticizer, as per the grading based on the compatibility of a plasticizer with base polymer [14].

Tensile properties

Results on the physico-mechanical properties of the vulcanizates are given in Table 3. An increase in the concentration of PCNSL from 10 to 20 phr

Table 2. Cure characteristics of the formulations at 150°C

Mix code	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}	U
Scorch time, t_{s2} (s)	101	146	131	109	120	124	109
Maximum cure, L_f (dNm)	40.5	26	15.3	50	47	44.8	53
Optimum cure time, t_{90} (s)	169	225	240	154	165	163	165
Cure rate (s^{-1})	1.5	1.3	0.9	2.2	2.2	2.6	1.8

Table 3. Physico-mechanical properties of the vulcanizates

Mix code	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}	U
Modulus-100% (MPa)	0.52	0.42	0.23	0.70	0.63	0.60	0.87
Tensile strength (MPa)	16.7	15.7	7.3	2.3	2.4	11.7	2.2
Elongation at break (%)	1060	1170	1340	300	330	840	240
Limiting oxygen index (LOI)	17.5	18	17.5	17	17.5	17.5	17

resulted in a reduction in the tensile modulus at 100% elongation of the vulcanizates from 0.52 MPa to 0.23 MPa (the value for the unmodified vulcanizate being 0.87 MPa). The corresponding reduction for the Santicizer modified vulcanizates was from 0.70 MPa to 0.60 MPa. This shows that a higher degree of softening or plasticization occurs with PCNSL as the plasticizer as compared to Santicizer at an equivalent dosage. The vulcanizate containing 10 phr of PCNSL in NR showed the highest tensile strength of 16.7 MPa as against 2.3 MPa for the NR vulcanizate containing the same dosage of Santicizer. The reduction in tensile strength for the PCNSL modified vulcanizates at higher concentrations of PCNSL indicates the lower extent of cure of these vulcanizates, as explained earlier [6], whereas a gradual increase in the tensile strength of the samples containing higher doses of Santicizer has been observed. However, the overall tensile strength observed with PCNSL modified mixes are much greater than that with Santicizer, due to the active participation of PCNSL in the network formation [17]. Though the elongation at break of all the vulcanizates increased with the increase in concentration of the plasticizer, the PCNSL modified vulcanizates showed comparatively higher elongations. The possibility for higher degree of interactions of the unsaturated side chain of PCNSL with NR and the probable formation of entangled network structures in the vulcanizates were held responsible for the higher tensile strength and elongation at break of the PCNSL modified NR vulcanizates [17].

Flame-retardancy

The results in Table 3 show a marginal improvement in the limiting oxygen index (LOI) of the PCNSL modified NR vulcanizates as compared to the Santicizer modified samples with the increase in content of plasticizer from 10 to 15 phr. However, when a phosphatic plasticizer is used alone, the increase in LOI obtained over the unmodified sample is not significant, as reported earlier [6, 18]. Generally, phosphorous flame retardants find their largest use in hetero-atom polymers, with the highest efficiency apparent in highly oxygenated polymers [19]. Thus, considerable improvement in flame retardancy with phosphatic flame retardants has been reported for cellulose, where the mechanism of flame retardance involves mainly the condensed phase reactions [19]. Reactive phosphorous flame retardants are used extensively in polyurethane foams, by virtue of their effectiveness in reducing flammability by char-forming condensed phase mechanisms [19]. However, significant increase in LOI along with self-extinguishing characteristics can be obtained for NR vulcanizates by modification with a brominated derivative of PCNSL [20, 21]. Further increase in the LOI of NR vulcanizates upto 42 could be achieved by synergistic combinations of brominated PCNSL with antimony trioxide [21].

Resistance to thermo-oxidative decomposition

The resistance to thermo-oxidative decomposition of the vulcanizates has been studied by measuring *[1]* the retention of tensile properties after accelerated ageing in a hot-air oven and *[2]* decomposition characteristics during dynamic thermogravimetry in air at different heating rates, the results of which are given in Table 4 and Table 5, respectively.

Effect of accelerated ageing on tensile properties

The results in Table 4 show the retention in tensile modulus, tensile strength and elongation at break of the NR vulcanizates after ageing at 70°C for 12 h. The superiority of PCNSL modified vulcanizates over that containing Santicizer, with respect to retention in tensile properties is quite obvious. The increase in the content of plasticizer from 10 to 20 phr, leads to a relatively higher retention in properties for the former, as against the latter. Improved retention in tensile properties of PCNSL modified NR vulcanizates after accelerated ageing has also been observed earlier [6] which was attributed mainly to post-vulcanization reactions leading to the formation of additional crosslinks [17]. The absence of unsaturation in the alkyl groups of 2-ethyl hexyl diphenyl phosphate (Santicizer) rules out the possibility of any chemical reactions with NR matrix, with the result that no additional crosslinks are formed as reported for PCNSL modified NR systems.

Dynamic thermogravimetry

The decomposition characteristics of the NR vulcanizates was studied by dynamic thermogravime-

Table 4. Retention in tensile properties of the vulcanizates after aging at 70°C for 12 h[a]

Mix code	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}	U
Modulus-100% (%)	103	103	110	99	101	106	101
Tensile strength (%)	76	93	118	71	78	17	96
Elongation at break (%)	90	96	99	73	79	33	95

[a] % of original.

Table 5. Decomposition characteristics of the vulcanizates-(TGA)

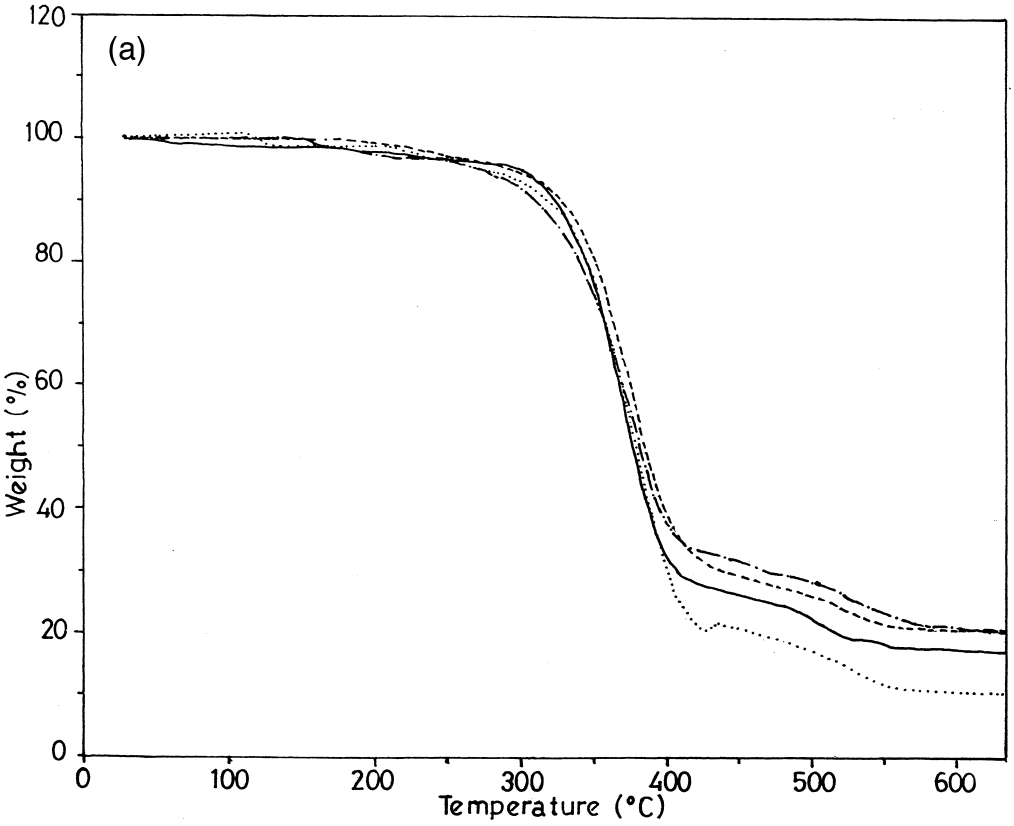
Heating rate (°C min^{-1})	Mix code	T_{50} (°C)	$T_{\max}$ (°C)	Rate of decomposition (% min^{-1})	Activation energy (kJ mol^{-1})	Residue at 600°C (%)
10	U	374	350	6.0	547.3	10.2
	P_{10}	365	340	5.8	421.4	15.3
	P_{15}	359	350	5.9	202.5	11.7
	P_{20}	369	350	5.4	146.4	16.8
	S_{10}	362	350	5.4	302.1	16.1
	S_{15}	344	330	5.3	118.3	14.2
	S_{20}	361	360	5.4	95.8	12.5
20	U	385	390	11.7	521.5	8.6
	P_{10}	385	380	11.9	315.8	11.2
	P_{15}	387	380	11.1	161.6	13.3
	P_{20}	387	380	10.7	108.7	11.2
	S_{10}	387	380	10.3	130.9	10.8
	S_{15}	366	360	11.3	88.1	9.8
	S_{20}	362	360	11.5	79.5	11.7
40	U	378	380	25.5	214.4	10.8
	P_{10}	377	370	26.2	261.8	17.7
	P_{15}	384	380	22.6	225.1	21.0
	P_{20}	381	380	21.8	117.9	21.2
	S_{10}	381	380	20.9	144.0	20.8
	S_{15}	380	380	21.4	135.2	14.1
	S_{20}	372	380	23.4	46.0	13.5

try. Since thermally induced polymer decomposition is the first step in the ignition process [21], a knowledge of the thermal and thermo-oxidative degradation of polymeric materials is essential for an understanding of the nature of decompositions occurring under pyrolytic conditions. Thus, results from a typical TGA curve give valuable informations on the thermal stability [22] in addition to the nature of decomposition and its kinetics [23]. The temperature at which 50% of the weight of a given polymer is vaporized under standard pyrolytic conditions (T_{50}) has been considered to be a quantitative measure for thermal stability [24]. The average rate of decomposition during the major degradation step gives an indication of the extent of volatile/flammable hydrocarbons liberated during pyrolysis. The magnitude of the activation energy for decomposition in this temperature range may be considered as a measure of the thermal stability/resistance to thermo-oxidative decomposition of the material. Positive correlation between oxygen index and char-yield from pyrolysis data has been reported earlier [25]. The rate of energy input (which in turn determines the rate of thermal decomposition) is a critical factor for polymer ignition [21]. Hence, the TGA was carried out at three different heating rates (10, 20 and 40°C/min) — the results of which are given in Table 5.

The results show a clear change in decomposition pattern and the kinetic parameters of decomposition with the increase in heating rate from 10 to 40°C/min. Thus, compared to the unmodified and Santicizer modified NR vulcanizates, the thermal stability of the PCNSL modified NR vulcanizates increases to a greater extent with the increase in heating rate. This is evident from the higher values of T_{50} of the PCNSL modified vulcanizates, particularly with 15 to 20 phr of PCNSL.

The activation energy for thermal decomposition of all the vulcanizates (in the temperature range from 310 to 360°C) decrease with the increase in heating rate. However, in all the cases, the values for the PCNSL modified vulcanizates are consistently higher than that of the Santicizer modified samples at similar dosages of the plasticizer. This again is an indication of the improved resistance to themo-oxidative decomposition of the PCNSL modified NR vulcanizates compared to that containing Santicizer.

The average rate of decomposition of the vulcanizates in the initial major decomposition region (from 310°C to 380°C), increases from around 6%/min at a heating rate of 10°C/min, to above 20%/min at the heating rate of 40°C/min. However, above the heating rate of 20°C/min, a change in the decomposition pattern is discernable between the vulcanizates containing PCNSL and the Santicizer; the rate of decomposition of the former decreases with the increase in content of plasticizer against an increase under the same conditions for the latter (Fig. 2). Since the pyrolytic decomposition products of NR at the initial stages (mostly of the flammable hydrocarbon type) contributes greatly to its flammability, the reduction in the rate of liberation of such products for the PCNSL modified NR vulcanizates, is thought to be partly responsible for their better flame retardancy compared to Santicizer modified vulcanizates. This is further supported by the higher values of LOI and higher yields of decomposition residue of the former, compared to that of the latter. The above results, particularly the reduction in rate of decomposition and increase in solid decomposition residue of NR vulcanizates containing higher concentrations of PCNSL, at higher heating rates indicates the probable changeover of the mechanism of decomposition of NR from a free radical type to one involving a higher degree of condensed phase reactions, typical of phosphatic flame retardants. The significance of this can be better appreciated while considering the nature of a fire situation where the rate of heat release is often of a very high order.



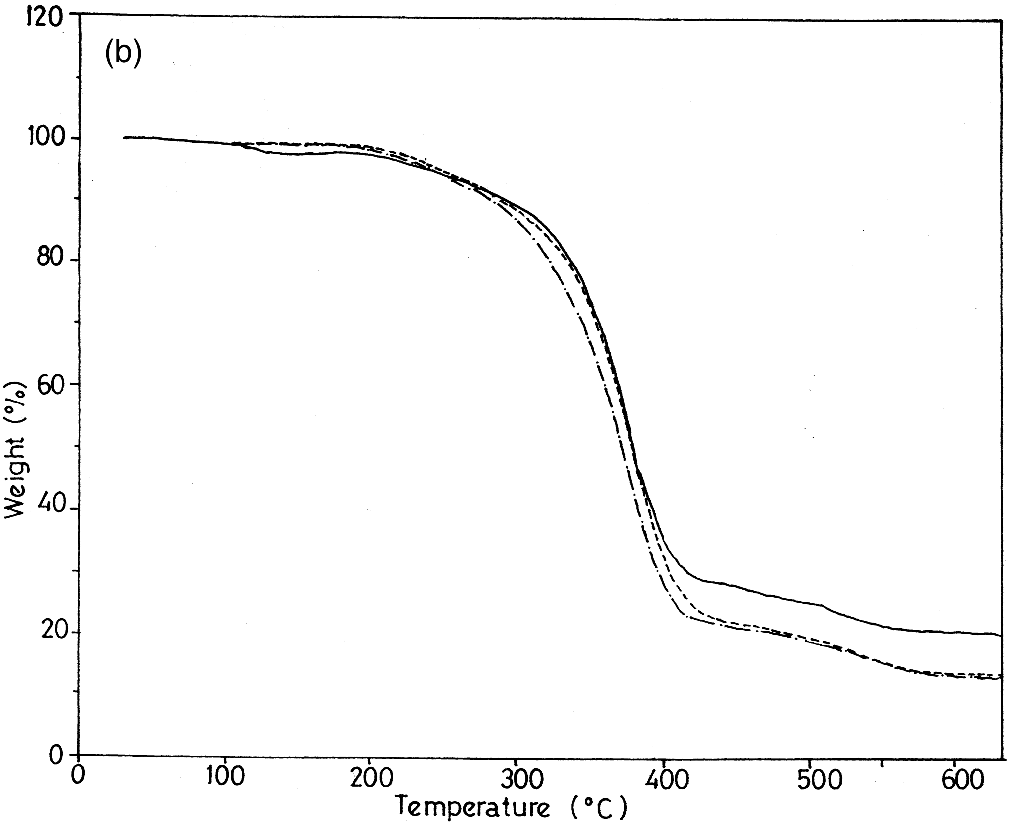


Fig. 2. (a) TGA of unmodified and PCNSL modified NR vulcanizates. (b) TGA of Santicizer modified NR vulcanizates.

CONCLUSIONS

The results as enumerated above lead to the following conclusions:

(1) At equivalent dosages of the phosphatic plasticizers, the NR modified with PCNSL shows a higher degree of cure-retardation compared to those containing Santicizer.

(2) PCNSL imparts a higher degree of softening effect to the NR vulcanizates along with better tensile properties,flame retardancy and resistance to thermo-oxidative decomposition, compared to that containing similar dosages of 2-ethyl hexyl diphenyl phosphate (Santicizer).

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