Characterization of a Flame Retardant Plant Polymer and its Influence on the Properties of Rubber Vulcanizate

S. N. Ghosh[a]; A. K. Ghosh[a]; B. Adhikari[a]; S. Maiti[a]

[a] Materials Science Centre, Indian Institute of Technology, Kharagpur

PLEASE SCROLL DOWN FOR ARTICLE

Characterization of a Flame Retardant Plant Polymer and its Influence on the Properties of Rubber Vulcanizate

S. N. GHOSH, A. K. GHOSH, B. ADHIKARI* and S. MAITI

Materials Science Centre, Indian Institute of Technology, Kharagpur-721302

A renewable polymer, collected as a gum from a local plant (Moringa Oleifera) was characterized by various techniques *viz.* solubility, viscosity, IR, elemental analysis *etc.* It was compounded with various elastomeric systems *viz.* natural rubber (NR), nitrile rubber (NBR) and chloroprene rubber (CR) in order to judge its compatibility in the base polymers. 200% and 300% moduli, tensile strength, elongation at break (%) and hardness of the vulcanizates were measured. Surface morphology of the tear tensile specimen was studied by scanning electron microscopy (SEM). Retention of the above mechanical properties after leaching with boiling acetone for 48 h, with water at 30°C for 48 h and isothermal aging at 100 ± 2°C for 72 h of the samples was also measured. The results were compared with those of a non-polymeric fire retardant additive, Sb_2O_3, in an identical condition, as the plant polymer has shown potential fire retardant properties. Results indicated that the plant polymer-rubber blends showed, in general, improved retention of tensile properties before and after aging and leaching.

Keywords: Renewable polymer; Tensile strength; Fire retardancy; Scanning electron microscopy; Aging

INTRODUCTION

The term polymer blend refers to an intimate mixture of two or more polymers. The individual components may be melt mixed, solution

---

*Corresponding author.

blended and coprecipitated, or polymers in the latex form may be blended and coagulated before final processing. Though in many cases incompatibility or inhomogeneity arises, nevertheless many polymer blends perform well in new applications for which the individual blend components are not suitable. The blending of two or more structurally dissimilar polymers provides a convenient route for manipulation of properties to meet specific needs [1 – 3]. The mechanical blends are the most important class of polymer blends [4 – 6].

The blending of synthetics with natural polymers offers the potential of preparing new engineering materials with specific and improved properties for a wide range of applications, because such blends are expected to exhibit good properties of natural and man-made materials. For example, in continuation of our search for renewable resources for polymers we have recently reported the adhesive performance, flame retardancy and biodegradability of a plant polymer (PPP), obtained as a gum from a local plant (Moringa Oleifera), in blends with both natural and synthetic polymers [7]. On investigation it was found that the PPP contains about 4.34% phosphorus. As phosphorus compounds are known to have fire retarding property in polymers [8], the presence of phosphorus in PPP may be the cause of its fire retardant properties. The main aim of this investigation is to characterize and to evaluate the performance of this plant polymer (PPP) blends with various rubbers towards leaching and aging environments and to highlight its effectiveness as a fire retardant (FR) additive in comparison to the conventional FR additive, Sb_2O_3.

EXPERIMENTAL

Materials

Natural rubber (RMA-1), NBR (Paracryl CZLT, 40% ACN content), neoprene WRT were used as received. Sb_2O_3 (Aldrich Chem, USA), N-cyclohexyl benzthiazyl sulfenamide (CBS; ICI, India), zinc oxide (E. Merck), carbon black (N330) (Philips Carbon Black Ltd.), spindle oil (MCI), stearic acid (LR, Wilson Laboratory), sulfur (LR, Qualigens), ethylene thiourea (Na-22) (Du Pont, USA) were used as obtained.

Characterization of the Plant Polymer

The plant polymer obtained as a gum has been analyzed by solubility, elemental analysis, viscosity, IR, UV-visible, ^{1}H-NMR spectroscopy, TGA and DTA.

pH Measurement

20 cc DMAC solution of PPP (0.65%), 10 cc deaerated distilled water and 10 cc dehydrated alcohol were mixed and shaken well. A clear solution appeared and the pH measurement of this solution was carried out by a pH meter (EC, Model 5662) at 30°C. The measurement time was allowed until a constant pH was obtained.

I$_2$-Test

The iodine value provides a measure of the degree of unsaturation of the PPP. 20–30 mL of the solution of PPP in DMAC (0.2–1.0 g) was added to 25 mL of commercial Wij's solution (iodine trichloride + iodine + glacial acetic acid) in a 300 mL conical flask. The flask was stoppered and kept in the dark for 30 minutes. 10 mL of 20% aqueous potassium iodide solution and 100 mL distilled water were added and back titrated the excess iodine with 0.1 N sodium thiosulphate using starch as indicator. A blank test was also run using the same volumes of chloroform and Wij's reagent.

$$\text{Iodine Value} = 12.69 \times [\{(B - A)N\}/W]$$

where, A = mL $Na_2S_2O_3$ required to titrate the sample, B = mL $Na_2S_2O_3$ required to titrate blank, N = normality of $Na_2S_2O_3$, and W = g sample used.

Compounding

Compounding of various gum and filled stocks of different diene rubbers with the PPP and commercial FR additive Sb_2O_3 was carried out separately following standard laboratory procedure of ASTM D

15–54 T on a two-roll rubber mixing mill at $\sim 50 \pm 5°C$ for 15 minutes for gum stocks and $\sim 60 \pm 5°C$ for 20 minutes for filled stocks.

Curing of Rubber Stocks and Preparation of Testing Specimens

About 35 g of the compounded stock, gum or filled, after 24 h of mixing was put in a 15 cm × 10 cm mold with a cavity of 0.2 cm in a Carver hydraulic press (model 2518) with heating arrangement. Curing of all the stocks was carried out at 150°C under 8 ton pressure for optimum cure time (t_{90}) as determined previously from the rheometric study with a Monsanto Rheometer (R-100). The mold was preheated to the curing temperature in the closed press for at least 30 minutes and the mold cavity was sprayed with a silicone mold release agent before uncured stock was put into it. After curing the vulcanized sheet was immediately cooled under tap water to stop post curing.

Testing of Surface Morphology of the Rubber Compounds

The SEM micrographs of the tear surface of tensile specimens from rubber blends were studied by Cam Scan II, SEM micrograph at room temperature with a resolution of 500.

Physical Testing

Tensile properties *i.e.*, 200 and 300% moduli, tensile strength and elongation at break (%) were measured with a tensile testing machine (KMI Model 1.3 D) following ASTM D 412–51T. Prior to testing all the samples were conditioned for 48 h after vulcanization. Cure characteristics of all the rubber compounds were evaluated with Monsanto R-100 Rheometer. Scorch time and optimum cure time (t_{90}) were obtained from respective rheographs of the vulcanizates.

Isothermal Aging

Isothermal aging was carried out on vulcanized tensile specimens at $100 \pm 2°C$ using a forced air circulating aging oven for 72 h.

Solvent Leaching

Vulcanized tensile specimens were separately leached in boiling acetone and water at 30°C for 48 h.

RESULTS AND DISCUSSION

Analysis and Characterization of the Plant Polymer
Source of the Plant Polymer

The plant polymer is an exudate of the local plant (Moringa Oleifera). It was collected as a gum. The fresh gum collected directly in DMAC was filtered. The filtrate was dried at 60°C under vacuum. The dry product was used for analysis and characterization. Fresh gum was preserved under alcohol or formalin solution.

Physical Characteristics

(i) The plant polymer in the form of fresh gum collected from the tree is colorless which slowly becomes deep red and hard on exposure to air and light.

(ii) The stickiness of the fresh gum disappears when it becomes hard on exposure to air.

(iii) When the hardened gum is ground, its solution shows better adhesiveness.

(iv) The gum is of low molecular weight polymer (intrinsic viscosity 0.72 dL/g).

(v) The number average $(\overline{M}_n)$ and weight average $(\overline{M}_w)$ molecular weight are found to be 6630 and 9268 respectively. Polydispersity of the polymer is 1.39.

Solubility Behavior

PPP samples (0.02 g) were placed in test tubes containing 2 mL of different solvents and allowed to stand for two weeks. The polymer was then observed in order to judge the solvent effects such as swelling or dissolution. The results are shown in Table I. The fresh gum is

TABLE I Solubility behavior of the plant polymer (PPP)

Solvent	Solubility[a]	Solvent	Solubility[a]
Water	±	DMF	±
Alcohol	±	DMF + LiBr	+
MeOH	−	DMAC	±
Acetone	±	DMAC + LiBr	+
MEK	−	NMP	±
HCl	±	DMSO	±
HNO$_3$	±	HMPA	±
H$_2$SO$_4$	degrades	Toluene	−
HCOOH	±	Benzene	−
CH$_2$Cl$_2$	±	Pet-ether	−
CH$_2$ClCH$_2$Cl	−	Alcohol/toluene	±
CHCl$_3$	−	Cyclohexanone	−
CHCl$_2$CHCl$_2$	−	Amyl acetate	−
CCl$_4$	−	Amyl alcohol	−
Chlorophenol	−	Ethyl acetate	−
Benzene/acetone/ methanol (40:30:30) (V/V)	±	Toluene/methanol/ acetone (40:30:30) (V/V)	±

[a] + soluble; ± partially soluble; −insoluble.

partially soluble in water, acetone, alcohol, other polar aprotic solvents, and a mixture of solvents and is soluble in DMAC and DMF with 0.1% LiBr.

Viscosity Measurement

Inherent viscosity measurement of the plant polymer of 0.4%, 0.2% and 0.1% (w/v) solution in DMAC at 30°C was carried out using a Ubbelohde suspended level viscometer and the intrinsic viscosity is found to be 0.72 dL/g.

Elemental Analysis

The elements carbon and hydrogen present in the PPP were analyzed by Heraeus Carbo Erba 1108 elemental analyzer and phosphorus was estimated by the Schoniger Combustion Flask Method as followed by Schoniger [9]. Results of the elemental analysis of the plant polymer (PPP) are presented in Table II. It is evident from the Table II that the plant polymer contains higher percentage of oxygen and also some percentage of phosphorus. The presence of phosphorus in the polymer

TABLE II   Elemental analyses and the acid character of the plant polymer

Elemental composition (%)				pH of the DMAC solution of the PP
C	H	O	P	
41.77	5.65	48.24	4.34	5.80

indicates its flame retarding behavior [8]. The pH value (Tab. II) also indicates the acidic nature of the sample.

I$_2$-Test

Test for unsaturation was carried out by estimating the I$_2$ value. The I$_2$ value is found to be 13.96. This result indicates the presence of some unsaturated carbon atom in the backbone of the plant polymer.

IR Spectroscopy

IR-spectrum of the plant polymer powder was taken with a Perkin-Elmer 883 spectrophotometer in a KBr pellet. The IR spectrum is shown in Figure 1 and important peaks are assigned [10, 11] in Table III. The peak at 3326 cm^{-1} is assigned to the hydrogen bonded O—H stretching which is polymeric in nature and a strong peak at 2829 cm^{-1} indicates the C—H stretching (symmetrical) of > CH$_2$ group. Similarly a strong absorption at 1697 cm^{-1} confirms the presence of the α, β-unsaturated carbonyl (> C=O) stretching. A weak band at 2733 cm^{-1} is assigned to the —CH stretching of —C—H group. A sharp absorption peak at 1011 cm^{-1} is the characteristics of the alkyl-aryl (R—O—Ar) ether linkage. The peaks at 1138 cm^{-1} and 1371 cm^{-1} may be assigned to the C—H (CH$_3$) deformation and the C—O stretching or the O—H bending of secondary alcohol.

^{1}H-NMR Spectroscopy

^{1}H-NMR spectrum of the plant polymer was recorded with a Bruker 200 MHz FT NMR spectrometer using DMSO-D$_6$ as solvent (Fig. 2).

The ^{1}H-NMR spectrum of the plant polymer indicates the presence of five types of aliphatic protons and absence of any aromatic proton. The chemical shift at 4.03 ppm (broad singlet) indicates the presence
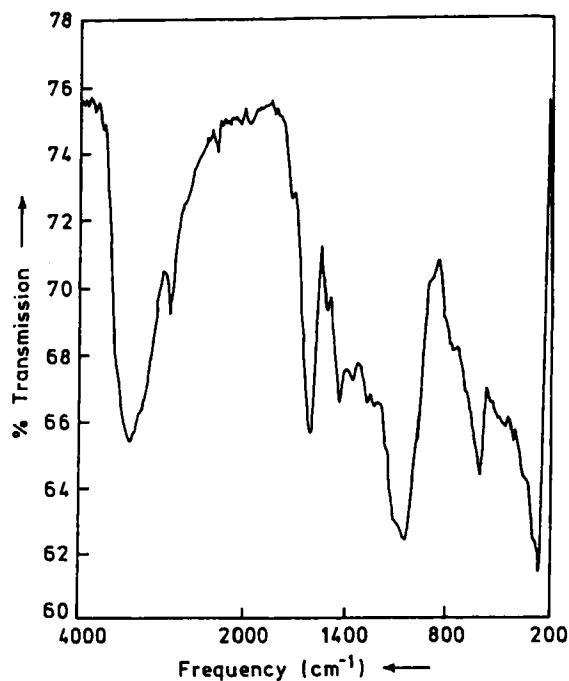
S. N. GHOSH *et al.*

FIGURE 1   IR spectrum of the plant polymer.

TABLE III   Important characteristic IR peaks of the plant polymer

Peak position cm^{-1}	Intensity	Assignment of peaks
3326	strong	H-bonded — OH stretching (Polymeric)
2829	strong	> CH_2 stretching (symmetric)
2733	weak	— C—H stretching of $\overset{\text{— C—H}}{\underset{O}{\parallel}}$ group
1697	strong	> C=O stretching (α, β-unsaturated)
1371	strong	C—H (CH_3) deformation
1138	strong	C—O stretching or O—H bending (secondary alcohol)
1011	strong	R—O—Ar linkage

of aliphatic O—H protons. From the broadness of the peak, it is suspected that they may be coupled with some olefinic unsaturated protons also. The other protons below 4.03 ppm indicate the presence of methyne, methylene or methylic protons which are adjacent to some
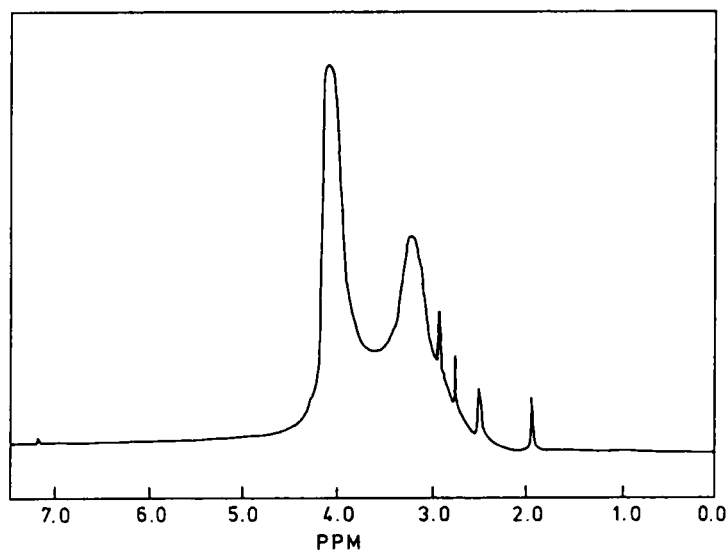
FIGURE 2 ^{1}H-NMR spectrum of the plant polymer.

deshielding environments such as, ether linkage, olefinic double bond *etc*. The presence of olefinic double bond is also supported by the positive response, though feeble, of I_2-test.

UV-visible Spectroscopy

UV-visible spectrum of the plant polymer was recorded with a Shimadzu UV-3100 spectrophotometer in DMAC solution (Fig. 3). Absorption maximum at 282 nm indicates the presence of α, β-unsaturated carbonyl or π-π^* transition of the benzene ring [10]. As from ^{1}H-NMR spectrum aromatic rings are absent in the plant polymer structure, the peak at 282 nm may be due to the α, β-unsaturated carbonyl.

Thermal Analysis

Both TGA and DTA thermograms of the PPP were recorded with a Shimadzu DT-40 thermal analyzer in air at a heating rate of 10°C/min. Both the thermograms are shown in Figure 4. As the complete structure analysis of the PPP has not been done here, so only
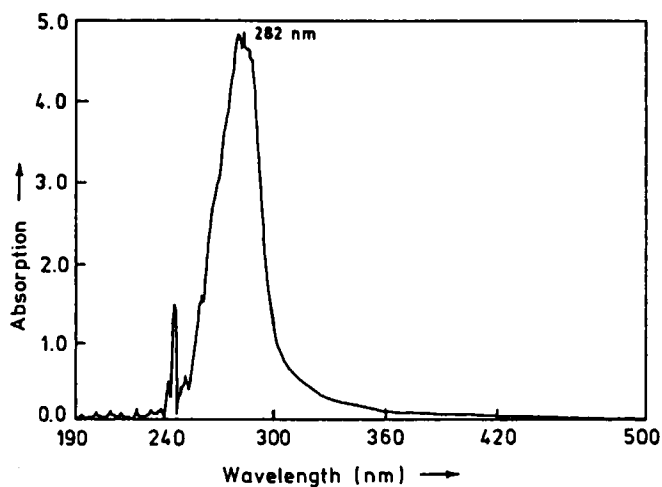
FIGURE 3   UV-visible spectrum of the plant polymer.
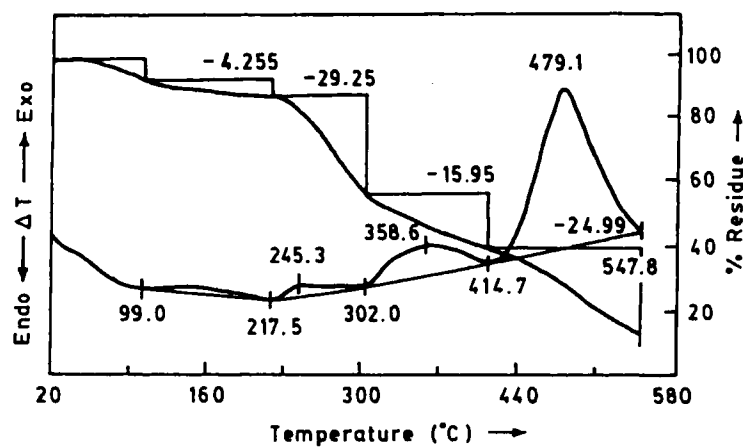
FIGURE 4   TGA and DTA thermograms of the plant polymer.

qualitative information can be reported from these thermal investigations. Possible informations from TGA and DTA of the plant polymer are presented in Table IV. Initial weight loss of about 5% occurs between 40 to 99°C and it is due to the loss of absorbed moisture. From the TGA and DTA curves it is evident that polymer undergoes mainly a four-step degradation. The plant polymer undergoes loss in

TABLE IV Thermal behavior of the plant polymer

TGA study			DTA decomposition temperature		
Temperature (°C)	% weight loss	Possible nature of weight loss	Initial temp. (°C)	Final temp. (°C)	Peak temp. (°C)
40–99	5.20	water or volatile loss			
99–217	4.25	degradation before melting	99	217	156
217–302	29.25	oxidative degradation	217	302	245
302–414	15.95	oxidative degradation	302	414	358
414–547	24.99	oxidative degradation	414	547	479

weight before melting which is also visually observed from the nature of the sample when burnt in a bunsen burner. The first degradation, besides moisture loss, may be due to some sort of condensation reaction between OH and COOH groups present in the PPP. The second degradation of the polymer occurs within 217 to 302°C which may be due to the oxidative degradation. 3rd and 4th steps also indicate degradation of the plant polymer. The plant polymer gives a char residue of 17% at 547°C. The little higher char residue is probably due to the presence of unsaturation in the polymer. This is expected to form some sort of crosslinking and thereby prevents complete loss by degradation. From DTA it is evident that all the peaks are exothermic in nature.

Tensile Properties of the Polyblends with Rubbers

The results of tensile properties are shown in Table V for NR, NBR and CR vulcanizates respectively. The tensile strength, 200 and 300% moduli and elongation at break remain either more or less constant or in some cases increase marginally for the vulcanizates in presence of the PPP used as a FR additive. The main drawback of the conventional FR additives is their tendency for migration and leaching in contact with solvents and even in air. Due to the polymeric nature the plant polymer shows better compatibility and leaching resistance when blended with other polymers. Therefore, the tensile properties of all the rubber compounds with Sb_2O_3 and the plant polymer were tested in a tensile tester using standard specimen dimensions. All these results are described in Table V.

TABLE V   Mechanical properties and LOI values of various rubber blends with the plant polymer (filled vulcanizates)[a]

Vulcanizate properties	Vulcanizate composition (phr)								
	NR (100)	NR/ Sb_2O_3 (100/5)	NR/PPP (100/10)	NBR (100)	NBR/ Sb_2O_3 (100/5)	NBR/ PPP (100/10)	CR (100)	CR/ Sb_2O_3 (100/5)	CR/PPP (100/10)
200% Modulus (MPa)	3.1	3.3	3.0	2.9	3.2	2.8	4.4	4.9	5.0
300% Modulus (MPa)	5.9	5.8	5.9	7.9	8.0	7.8	12.9	13.5	13.2
Tensile Strength (MPa)	16.8	16.5	16.9	16.7	15.5	16.9	13.5	14.7	15.5
Elongation at break (%)	480	470	480	450	440	470	340	350	350
Hardness (Shore A)	68	67	66	66	66	65	73	74	72
LOI	18.0	19.6	19.8	18.5	19.2	18.9	25.0	30.5	31.5

[a] Base formulation (phr): ZnO: 5, stearic acid: 2.0, C-black (N330): 40, spindle oil: 5, CBS: 2.0, sulfur: 1.5. In case of CR vulcanizates CBS was not used but MgO: 4 (phr) and Na-22: 0.5 (phr) were used.

Flame Retardancy of the Plant Polymer–Rubber Blends

Flame retardancy study of the PPP blends with different rubbers was carried out by limiting oxygen index (LOI) test. The test samples having the dimensions 15 cm length, 0.8 – 1.0 cm width and 0.2 – 0.3 cm thickness were cut following the standard specifications. The test specimens were burnt in a Stanton Redcroft FTA-Flammability Tester under controlled nitrogen/oxygen environments. Results are included in Table V. Flame retardancy of all the rubbers is enhanced, although marginally due to fire retardancy effect of the plant polymer. But the effect of this FR additive is excellent in case of neoprene rubber. This may be due to the synergistic effect of chlorine with phosphorus present in the plant polymer [12, 13]. To compare the flame retardancy of the plant polymer blends with rubbers, the most commonly used FR additive Sb_2O_3 has been used at 5 phr level.

Leaching and Aging Effect on Tensile Properties of Rubber Compounds

The percent retention properties of the rubber compounds with respect to the control specimen after leaching with water and acetone and aging at $100 \pm 2°C$ are shown in Tables VI – VIII, respectively. On an average the retention of tensile properties of NR, NBR and CR

TABLE VI   Water leaching resistance of various rubber vulcanizates (filled)

Blend composition[a]	Percentage retention of vulcanizate properties[b]				
	200% Modulus	300% Modulus	Tensile strength	Elongation at break	Hardness
NR	85	85	95	96	92
NR/Sb$_2$O$_3$	88	90	91	94	93
NR/PPP	93	98	93	98	95
NBR	88	89	85	91	91
NBR/Sb$_2$O$_3$	87	94	—	—	94
NBR/PPP	93	95	96	98	93
CR	90	90	90	89	91
CR/Sb$_2$O$_3$	91	88	92	94	91
CR/PPP	97	99	90	96	90

Leaching conditions: Water at 30°C, 48 h.
[a] Blend compositions are same as given in Table V.
[b] Each result is an average of three replicate experiments.

TABLE VII   Acetone leaching resistance of various rubber vulcanizates (filled)

Blend composition[a]	Percentage retention of vulcanizate properties[b]				
	200% Modulus	300% Modulus	Tensile strength	Elongation at break	Hardness
NR	81	83	81	80	89
NR/Sb$_2$O$_3$	79	88	76	90	91
NR/PPP	83	85	92	93	90
NBR	76	81	81	90	88
NBR/Sb$_2$O$_3$	77	85	89	93	93
NBR/PPP	89	95	92	95	94
CR	75	85	82	92	93
CR/Sb$_2$O$_3$	91	80	90	93	92
CR/PPP	97	98	92	92	90

Leaching conditions: Boiling acetone 48 h.
[a] Blend compositions are same as given in Table V.
[b] Each result is an average of three replicate experiments.

TABLE VIII   Aging resistance of rubber vulcanizates (filled)

Blend composition[a]	Percentage retention of vulcanizate properties[b]				
	200% Modulus	300% Modulus	Tensile strength	Elongation at break	Hardness
NR	89	86	95	90	90
NR/Sb$_2$O$_3$	93	85	· 90	89	92
NR/PPP	93	87	95	91	94
NBR	90	92	91	93	91
NBR/Sb$_2$O$_3$	94	95	95	93	90
NBR/PPP	96	94	96	95	93
CR	91	97	95	90	94
CR/Sb$_2$O$_3$	93	90	96	87	95
CR/PPP	95	97	95	83	92

Aging conditions: 100°C, 72 h.
[a] Blend compositions are same as given in Table V.
[b] Each result is an average of three replicate experiments.

compounds with this plant polymer (after leaching or aging) is superior to those of vulcanizates with and without Sb$_2$O$_3$. Around 6–8% increment of the percent retention value of the tensile properties was observed for the compositions containing plant polymer. This may be explained on the basis of better compatibility of these rubbers with the PPP. The vulcanizate properties of NR, NBR and CR with PPP after air aging at 100±2°C for 72 h (Tab. VIII) indicate that the plant polymer may also act as an antioxidant in those rubbers. Further studies are in progress to establish the antioxidant property of the plant polymer in rubber.
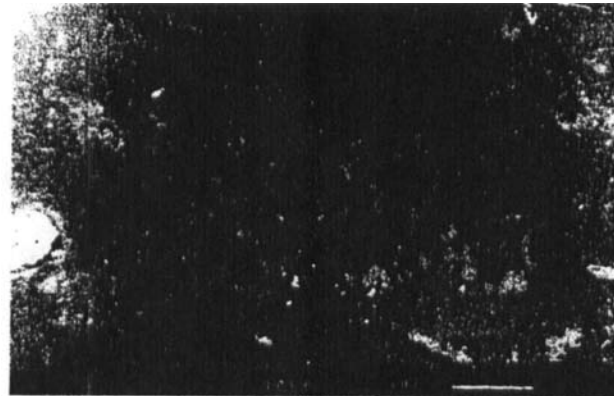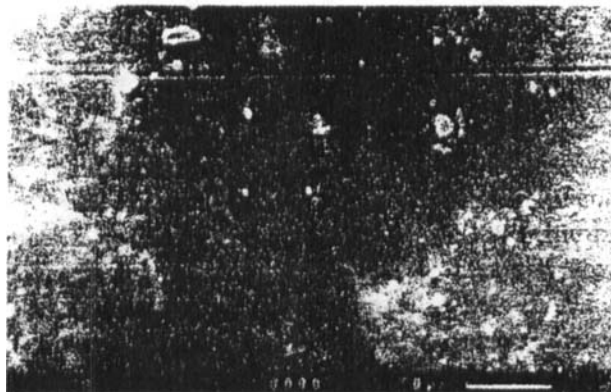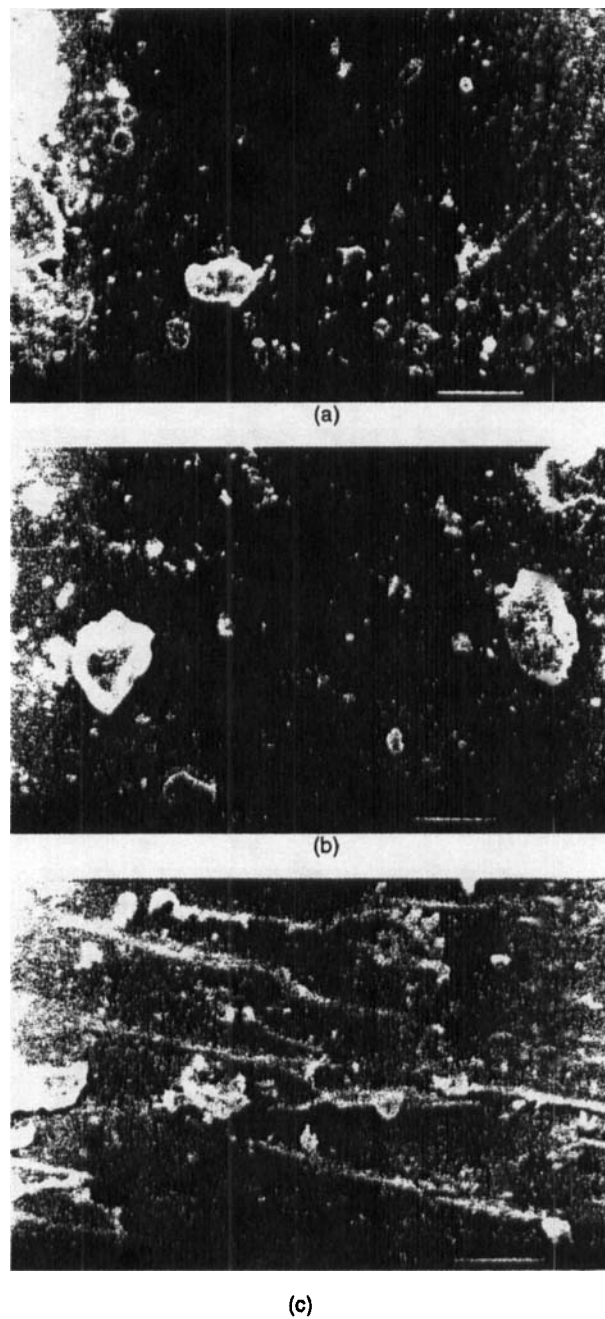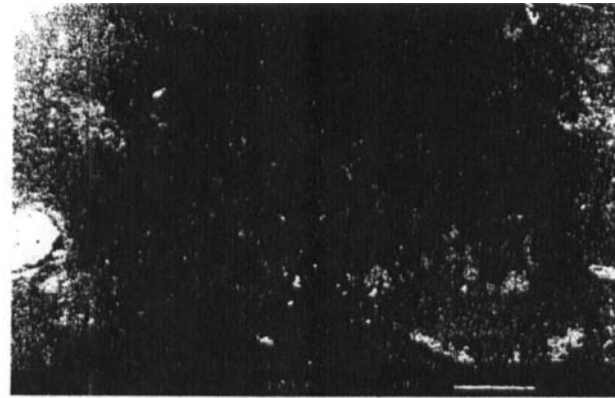
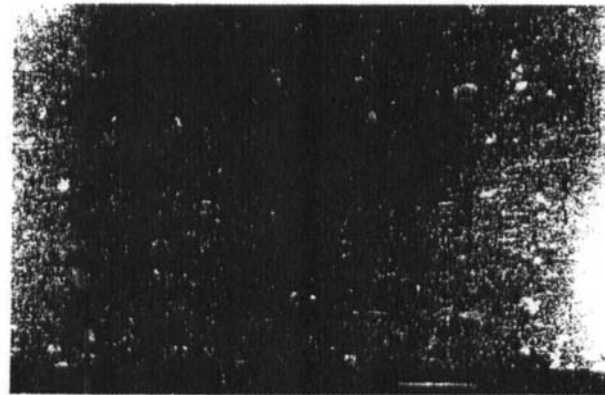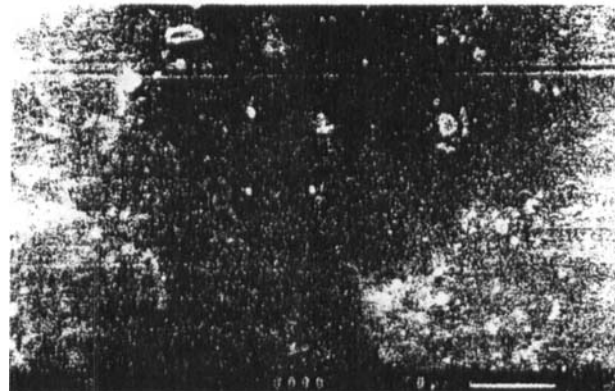FIGURE 5   SEM Photomicrographs of virgin polymers (a) NR, (b) NBR and (c) CR (gum vulcanizates).

FIGURE 6   SEM Photomicrographs of polymers containing Sb_2O_3 (a) NR, (b) NBR and (c) CR (gum vulcanizates).

(a)

(b)

(c)

FIGURE 7   SEM Photomicrographs of polymers containing plant polymer (a) NR, (b) NBR and (c) CR (gum vulcanizates).

Study of the Surface Morphology
of the Rubber Blends

The SEM photomicrographs of virgin NR, NBR and CR vulcanizates (gum vulcanizate) are shown in Figure 5 (a, b and c respectively), those of vulcanizates containing Sb_2O_3 are shown in Figure 6 (a, b and c respectively) and those of the rubbers blended with the plant polymer are shown in Figure 7 (a, b and c respectively). It is observed from the SEM study that the plant polymer exhibits better dispersibility than that of Sb_2O_3 as FR additive into the rubber matrices. Except NR (Fig. 7a), homogeneous surface morphology of all the rubbers blended with the plant polymer is observed. This may be due to better interaction of the polar plant polymer with the polar rubbers like NBR and CR and is reflected in other properties like tensile strength, hardness, *etc.*

CONCLUSION

The PPP has very specific solubility in DMF and DMAC containing 0.1% LiBr. From IR, ^{1}H-NMR and UV-visible spectra, it can be predicted that the plant polymer contains the 'mer' unit having some polar functionalities like —OH, α, β-unsaturated carbonyl, ether bridge *etc.* The polymer does not have any aromatic moiety. The phosphorus found in the plant polymer may be present as end groups in the polymer backbone. But the polymer structure can not be elucidated without further study like mass spectral analysis, FTIR *etc.* SEM study of the tear tensile specimen surfaces of NR, NBR and CR blends with PPP reveals that plant polymer can distribute itself well in NBR and CR matrices and gives homogeneous surface morphology. There is a problem of dispersion of PPP into NR matrix which may be due to less interaction of nonpolar NR with highly polar PPP. Tensile properties remain either more or less constant or in some cases increase marginally for the vulcanizates containing 10 phr of PPP used as FR additive. The retention of tensile properties of NR, NBR and CR compounds with this plant polymer is superior to those of vulcanizates with and without Sb_2O_3. This may be explained on the basis of better compatibility of these rubbers with the polymeric additive (PPP).

References

[1] Keskula, H. (1967). "Polymer Modification of Rubber Plastics", Wiley-interscience, New York.

[2] Bruins, P. F. (1970). "Polyblends and Composites", Wiley Interscience, New York.

[3] Carraher, C. E. Jr. and Moore, J. A. (Eds.) (1983). "Modification of Polymers", Plenum Press, New York.

[4] Work, J. E. (1973). *Polym. Eng. Sci.*, 13, 46.

[5] Krause, S. (1972). *J. Macromol. Sci. Rev. Macromol. Chem.*, 7, 251.

[6] Paul, D. R. and Newman, S. (Eds.) (1978). "Polymer Blends", Vol. 1, Academic Press, New York.

[7] Ghosh, S. N. and Maiti, S. (1998). *Eur. Polym. J.*, 34, 849.

[8] Stephens, H. L. (1986). "Rubber Technology", Morton, M. (Ed.), Van Nostrand Reinhold Company, New York, p. 20.

[9] Schoniger, W. (1955). "Schoniger Oxygen Flask Technique", *Microchim Acta*, p. 123; *ibid* (1956), p. 869.

[10] Dyer, J. R. (1994). "Application of Absorption Spectroscopy for Organic Compounds", 5th edn., Prentice Hall, New Delhi.

[11] Vogel, A. I. (1984). "Text Book of Practical Organic Chemistry", 4th edn., ELBS, Longman.

[12] Cullis, C. F. and Hisschler, V. (1981). "The Combustion of Organic Polymers", Clasender Press, Oxford.

[13] Pitts, J. J. (1973). "Flame Retardancy of Polymeric Materials", Kuryla, W. C. and Pappa, A. J. (Eds.), Marcell Dekker, New York, 1, 133.