LIGNIN REINFORCED RUBBER COMPOSITES

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Abstract

Lignin is the country's second most abundant renewable biomass resource next to cellulose. The pulp and paper industries produce very large quantities of lignin, most of those are burned to recover energy, pulping chemicals, enzymatic or acid hydrolysis to sugars followed by fermentation to alcohols. Another emerging technology where the lignin being used is in the adhesives and asphalts. For the former, lignin partly replaces phenol in phenol-formaldehyde formulations, for the latter lignin is used as an extender. Lignin in polyurethanes is for good mechanical properties and reactions of lignins such as grafting and crosslinking agent are also well known.

Novolak-hexamine based phenolic resins are commonly used as reinforcing and processing aids in nitrile rubber (NBR) compounds. Not only the oil and petrol resistances increase significantly, resin loading is also found to offer better heat resistant properties than carbon blacks. For seals, valves and gasket applications addition of phenolic resins provides superior abrasion resistance, ageing and negligible hardening effects at elevated temperatures. Poor tackiness of NBR compounds can easily be eliminated by using phenolic resin in place of carbon black.

The study presented here is to explore the possibility of employing lignin into some value-added rubber based composites. Lignin, gymnosperms, angiosperms and glass varieties, contain alcohol and phenolic groups and also double bonds in their structural moiety and therefore, could resinify into prepolymer in presence of hexamine. Varied proportions of lignin upto 50 parts with respect to total rubber plus hexamine, have been incorporated in medium acrylonitrile (37%) NBR and studied for their processing characteristics and physico-mechanical properties e.g. reinforcement, oil and fuel resistances, ageing and thermal stability. Efficacy of lignin has been found to be superior to either phenolic resin-hexamine or carbon black filled compounds. Finally, attempt has also been made to modify the surface chemistry incorporating C-O,>C=O etc. groups by additions of dicumyl peroxide and this modified lignin was found to offer improved rubber-filler adhesion, tackiness and physical properties.

Introduction

Lignin is the country's second most abundant renewable biomass resource next to cellulose. The pulp and paper industries produce large quantities of lignin, most of those are burnt to recover energy, pulping chemicals, enzymatic or acid hydrolysis to sugars followed by fermentation to alcohols. Another emerging technology where the lignin being used is in the adhesives [1] and asphalts [2]. For the former the lignin partly replaces phenol in phenol-formaldehyde formulations, for the latter lignin is used as an extender. Lignin in polyurethanes is for good mechanical properties and reactions of lignin such as grafting and crosslinking agents are also well known [3-5]

So far, only limited studies on the application of lignin as a filler in rubber vulcanizates have been made. Kumaran et al. [6-9] used lignin as a replacement of carbon black in styrene - butadiene and natural rubbers. Nichols [10] employed kraft lignin as a reinforcing agent in elastomeric composition based on polyethers, polyester amide and poly alkylene glycols. Physico-mechanical properties were reported to be improved for the final elastomeric product by using oxidised kraft lignin instead of lignin in the unmodified form. Haxs and Mills [11] have reported the possibility of development of lignin-reinforced rubber vulcanizates by co-precipitating lignin with rubber latex and subsequent treatment with an organic poly-isocyanate. Various lignin preparations as fillers in rubber vulcanizates have also been compiled by ACS Rubber Division library [12]. Nada [13] has investigated the possibility of using lignin separated from the spent liquor of soda pulping of rice and straw as a partial replacement of phenol in preparing resole type of resin. Venderklashorst [14] has observed that the reaction of formaldehyde with lignin in acid medium for meta substitution of the aromatic hydroxyl group and fast crosslinking in polymeric products. The reaction was also reported to be different in alkaline condition where the substitution occurred at position ortho or para to the aromatic hydroxyl group.

Novolak-hexamine based phenolic resins and carbon black are commonly used as reinforcing fillers in NBR vulcanizates. For seals, valves and gasket applications, addition of phenolic resins have been found to provide superior abrasion and heat resistance as well as improved tackiness for the gum compounds compared to using carbon black.

The study presented here is to explore the possibility of employing lignin into some value-added rubber based products. Lignin contains both alcohol and phenolic groups and also has double bonds in their aromatic structural moiety. These, therefore, possibly could resinify into prepolymer in presence of hexamine. Lignin plus hexamine have been incorporated into NBR and studied for their physico-mechanical properties, morphology and failure properties, oil and fuel resistances and thermal stability vis-a-vis those of phenolic resin plus hexa and carbon black filled vulcanizates.

Finally, an attempt has also been made to modify the surface properties of crude lignin to achieve better reinforcement and physical properties.

Experimental Procedure

Solutions of either 1 or 5 gms of dicumyl peroxide (DCP) in 10 ml acetone was thoroughly mixed with 100g of lignin. Acetone was removed from lignin by air drying for 24 hours at room temperature followed by heating at 150°C for one hour under nitrogen atmosphere and air separately in an oven and then allowed to cool in a dessicator.

The formulation of the mixes are given in Table-1. Mixing was carried out in a conventional laboratory open mill [150mm x 330mm] at 30-40°C according to ASTM method D 15-70. Different ingredients were added as per the sequence mentioned in the Table-1. Developed mixes were vulcanized for 30 min at 150°C and 200kg/cm² pressure in a hydraulic press having electrically heated platens. Specimens for tensile test were punched out along the grain direction from the vulcanized sheets. Tensile testing was done as per ASTM method D 412-51 T using dumb-bell specimens. This test enables to obtain elongation at break and modulus values of the vulcanizates.

Shore A type Durometer was employed to find out the hardness of the vulcanizates. Readings were taken after 15 seconds of the indentation when firm contact has been established with the specimen. The method adopted is the same as that of ASTM D 676-527 T.

Samples, having the dimensions of 12.5 mm thick and 28 mm dia were taken in duplicate and compressed to constant deflection (25%) and kept for 22 hours in an air oven at 70°C. After the heating period the samples were taken out and cooled at room temperature for half an hour and the thickness was measured. The compression set at constant strain was reported as per ASTM method D 395-61 method B.

Tear strength of the vulcanizates was determined using un-notched 90 degree angled tear test pieces (dieC) as per ASTM method D 624-48.

Samples of approx. 10 mm dia, 2.5 mm thick and 0.3g weight were cut from the central portion of the moulded sheet and allowed to swell in various oils and fuels at 35°C in thermostatically controlled water bath. Swollen samples were taken out after 72 hours, blotted with filter paper and weighed quickly in stoppered weighing bottle. Duplicate readings were taken for each sample and percentage of oil/fuel swelling was calculated.

NBR pellets mixed with either lignin or modified lignin and vulcanizates were

analysed for percentage transmittance on MAGNA-750 FTIR of NICOLET, USA.

TMA module 2970 with TA controller 3100 was utlized for evaluation of thermomechanical properties of the vulcanizates under static load (10g), rate of heating 10°C per min and maintained under nitrogen gas flow rate of 100 ml per min.

TGA module 2950 with TA controller 3100 was used for thermo-gravimetric analysis of the vulcanizate under nitrogen gas flow (60 ml per min) and heating rate 20°C per min in the thermal range 0 to 800°C.

The fractured surfaces of the tensile test specimens were cut carefully without touching the surface. Surfaces were subsquently sputter coated with gold within 24 hours of testing and studied under a JEOL 35 CF scanning electron microscope (SEM) for failure mechanism and phase morphology.

Results and Discussion

The mechanism of lignin action in NBR vulcanizates can be explained from physico-mechanical properties as enumerated in Table-2. Addition of lignin increased the structural complexity due to inefficient utilization of sulfur in cross link formation. Extra sulfur, however, caused main chain modification as pendent groups terminated with accelerator residue and higher zinc sulfide formation. Presence of lignin, therefore, caused improper vulcanization and also generates lower values of tensile strength and higher compression set compared to gum vulcanizate. Improvement in hardness and modulus values were primarily due to reduction in volume fraction of rubber for the 50 phr. filled lignin composition rather than any reinforcement. Modification of crude lignin by DCP (5%) improved surface reactivity due to conversion of phenolic or aliphatic OH into new functionalized groups like ketone or aldehyde etc. Improvement in tear strength, hardness, modulus and specially compression set occurred as a result of enhanced reinforcement by modified lignin in comparison to its crude version.

Mechanical properties for the phenolic resin + hexamine composition (mix C) can be explained from solution theory. Resin which is a semisolid in the ground state when added to NBR behaves like a solute. Absorption of resin by NBR, lowered the normal melting point of the resin (i.e., 40-50°C) below the room temperature. The resin filled composition, therefore, should be more flexible which is contrary to the list of physical properties shown in Table-2. Probably, in this case, excess resin at 50 phr. level, exceeds the solubility limit of NBR and integrity of the matrix is hampered. Further the NH_3 and HCHO which got liberated from hexamine in presence of H_2O in air underwent crosslinking with the resin and got crosslinked intermolecularly. All these accounted for higher tensile strength, tear strength, hardness, modulus values

compared to mixes A or B, at the same time reduction in elongation at break and higher compression set resulted.

Carbon black reinforced vulcanizate, as expected, was always superior to all and the observation is in accordance with the chain slippage mechanism of reinforcement or bound rubber theories.

Both phenolic resin and lignin are more polar than NBR. Excepting in ester type oil, the mixes B and C showed better swelling resistances compared to mix A. Carbon black in mix D generated efficient reinforcement and structural integrity and caused further improvement in swelling restriction in almost all the exposed environments. However, it is interesting to notice that wherever the high viscosity mineral oil and diesel exposure are considered, DCP modified lignin composition (mix E) was found to be the best.

Topographical features of the tensile fractured surfaces of the mixes B to E were studied under the SEM to understand the failure mechanism. Figure 1 is the SEM photograph of tensile fractured surface of lignin filled mix B. Inadequate filler-matrix adhesion caused pulling out of the filler agglomerates from the matrix during failure. Formation of pits, larger cavities and grooves signify poor tensile strength for this vulcanizate. With surface modification by reacting lignin with DCP, the reinforcement properties of the filler is changed. This is also evident in the surface morphology of mix E as observed in Fig.2. Extent of cavitation is reduced and the composite, therefore, showed better tensile properties than mix B. In the case of addition of resin (mix C), co-existance of resin-hexa and NBR phases were evident (Fig.3). Better filler-matrix adhesion caused neither dewetting nor cavitation. However, excess resin was separated out from NBR and formed a separate phase. Tensile strength was, therefore, improved marginally. Maximum improvement in the tensile strength was noticed in carbon black filled vulcanizate of mix D. Filler agglomerates in this case, were much smaller and properly adhered to the matrix (Fig.4).

FTIR studies also showed encouraging results. Fig. 5 shows the FTIR spectrum of the lignin used and its structural identification of various peaks are mentioned in Table-3. The spectrum was then compared with the standard library and found to resemble kraft lignin. Fig. 6 shows FTIR spectra of 1% and 5% DCP modified lignin respectively. Appearence of new functional groups with 5% DCP modification in the range of 1600-1700 cm^{-1}, not present originally in lignin, indicate formation of carbonyl functionality with peroxide at elevated temperatures. Fig. 7a is the FTIR spectrum of gum vulcanizate (mix A) showing sharp peaks at 2237 cm^{-1} (-CHCN), 1444 cm^{-1} (-CH2-), 975 cm^{-1} (-CH-CH- 1,2 vinyl). Addition of unmodified lignin into NBR showed masking of its characteristic peaks in the region between 1800 - 800 cm^{-1} (Fig. 7b). Appearance of a new peak at 2350 cm^{-1} and broadening of the acrylonitrile peak

intensity at 2237 cm^{-1} indicate polar-polar interaction or possibly hydrogen bonding between hydroxyl groups of lignin and acrylonitrile group of NBR. Surface modification and generation of active functionality due to DCP treatment improved reinforcement capability of the modified lignin. The FTIR spectrum (Fig. 7c), in this case, not only matches with pure NBR (Fig. 7a) but also showed sharper peaks in the region between 1800 - 800 cm^{-1} due to enhanced filler-matrix interaction.

Characterzation of temperature resistance of the material has diverse concerns such as dimensional stability on heat fluxes, thermal decomposition and determination of service temperature. TMA (Fig.8) shows the plots of the gum as well as filled vulcanizates. The modified lignin showed much lower dimensional changes and heat stability in the entire temperature range from -50°C to 175·C.compared to either phenolic resin or carbon black. Analyses of the TGA plots of the filled vulcanizates (Fig.9) showed different stages of decomposition for the lignin filled vulcanizate compared to those of either phenolic resin or carbon black. Maximum serviceable temperature is also obtained in case of lignin than others.

Conclussions

1. Country's renewable waste lignin, after suitable chemical treatment, has been found to be effective as a reinforcing filler in nitrile rubber.

2. Addition of modified lignin also resulted in better thermal stability for the vulcanizates compared to phenolic resin or carbon black.

3. Lignin has the capability of replacing costlier and petroleum based carbon black for applications where superior oil and fuel resistance characteristics of nitrile rubber are of primary concern.

References

1. R.L.Heming and A.H. Conner (eds.), Adhesives from Renewable Resources, ACS Symp. Ser. 385, Washington DC, 1989.

2. D.W. Sundstrom and H.E. Klei, Biotech. and Bioengg. Symp., **12** (1982) 45.

3. S.S.Kelley, W.G. Glasser and T.C. Ward, J. Appl. Polym. Sci., **36**, (1988) 759.

4. H.Yoshida, R.Morck, K.P. Kringstad and H. Hata Keyama, J. Appl. Polym. Sci., **40** (1990) 1819.

5. J.J. Meister and D.R. Damodar, J. Appl. Polym. Sci., **29** (1984) 3457.

6. M.G. Kumaran and S.K.De, Kautschuk Gummi Kunststoffe, **30** (1977) 915.

7. Idem, J. Appl. Polym. Sci., **22** (1978) 1885.

8.   Idem, Kautsichuk Gummi Kunststoffe, **31** (1978) 435.

9.   Idem, J. Polym. Sci., **17** (1979) 399.

10. R.R. Nichols, U.S. Pat. 2, 845, 422 (1958).

11. H.E. Haxs and G.S. Mills, U.S.Pat. 2, 906, 718 (1959).

12. Bibliography No. 109, ACS Rubber Division Library and Information Service, Univ. of Akron, Ohio, USA, 1971.

13. A.M.A. Nada, J. Appl. Polym. Sci., **23** (1987) 2915.

14. G.H. Vanderklashorst, Polymer Chemistry, **23** (1986) 2143.

Table 1
Formulation of Mixes

Ingredient	Mix Nos.				
	A	B	C	D	E
Nitrile rubber1	100	100	100	100	100
Zinc oxide	15	15	15	15	15
Stearic acid	1.5	1.5	1.5	1.5	1.5
Lignin2	—	50	—	—	—
Modified Lignin3	—	—	—	—	50
Phenolic Resin4	—	—	50	—	—
Carbon Black5	—	—	—	50	—
Hexamine6	—	5	5	—	5
Sulphur7	0.3	0.3	0.3	0.3	0.3
MBTS7	1	1	1	1	1
TMT7	3	3	3	3	3

1. NBR, Perbunan 3307, Bayer A.G., Germany

2. Crude Cellulosic waste obtained from pulp and paper industries of Kanpur

3. DCP modified lignin

4. PR 202, Rubber reinforcing resin, M/s Hard Castle Wand Ltd.,Bombay

5. SRF carbon black (N 765), obtained from Philips Carbon black Ltd., Durgapur

6. Hexamethylene tetramine, BDH, Germany

7. Commercial grades of sulphur, MBTS, TMT obtained from M/s Ailga Rubber Works, Kanpur

Table 2
Physical properties of the vulcanizates

Property	Vulcanizate No.				
	A	B	C	D	E
Tensile strength, kg/cm^2	23.3	15.4	54.3	156.0	15.6
Modulus at 100% elongation, kg/cm^2	1.0	10.9	52.9	20.6	13.0
Elongation at break, %	300	375	125	450	250
Tear Strength, kg/cm	12.0	12.3	41.3	57.5	14.3
Hardness, Shore A	40	55	85	55	60
Compression set, %	12.0	12.7	15.6	4.0	6.0
Volume swelling, %					
A. X-oil (High viscosity mineral oil)	2.12	1.03	1.65	0.09	-2.15
B. Ox-38 (Ester type oil)	0.24	0.35	0.73	0.00	0.89
C. Isooctane: Toluene 70:30 (Fuel)	0.83	0.64	0.72	0.52	0.86
D. Diesel	0.54	0.39	0.00	0.82	0.00

Table 3
Transmittance band / wave number of lignin and its structural assignment

Sl. No.	Wave Number (cm^{-1})	Structural assignment of lignin
1	3408.2	Stretching vibration of hydrogen bonded OH groups
2	2921.3	Tertiary -OCH$_3$ groups
3	1737.7	Acid or Ester carbonyl groups
4	1607.9	Conjugated aromatic ring
5	1377.9	Bending vibration of OH bonds
6	1253	Phenolic OH stretching
7	1164-1042	C-O stretching
8	897.7	1-2-5 substituted aromaticing
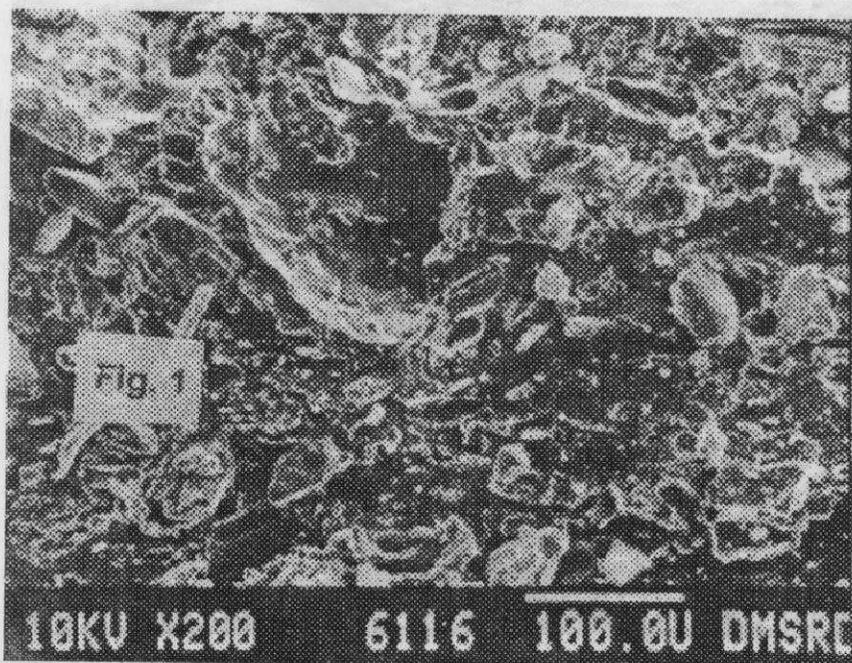
Fig. 1 - SEM photograph of Lignin filled vulcanizate of mix B
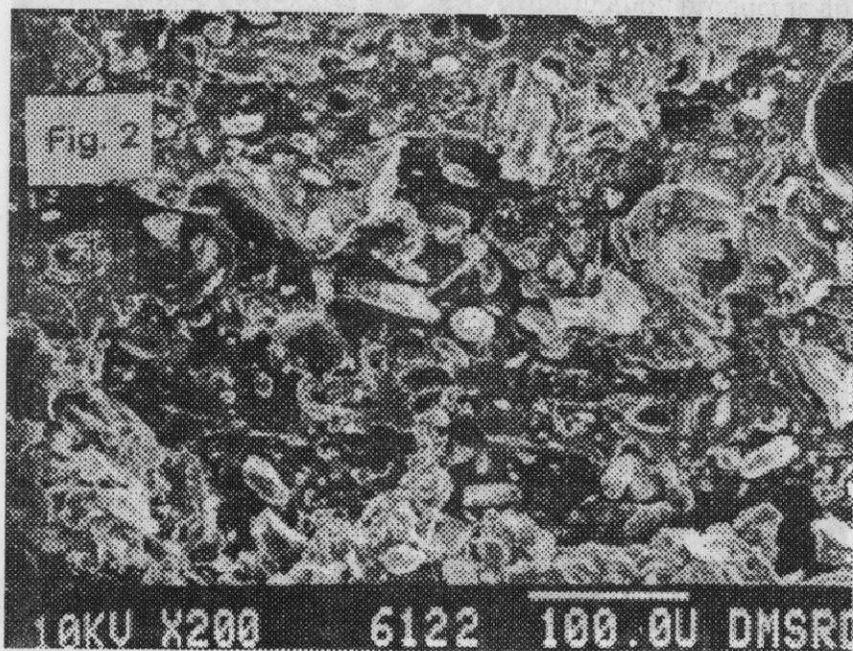
Fig. 1 - SEM photograph of DCP modified Lignin filled vulcanizate of mix E.
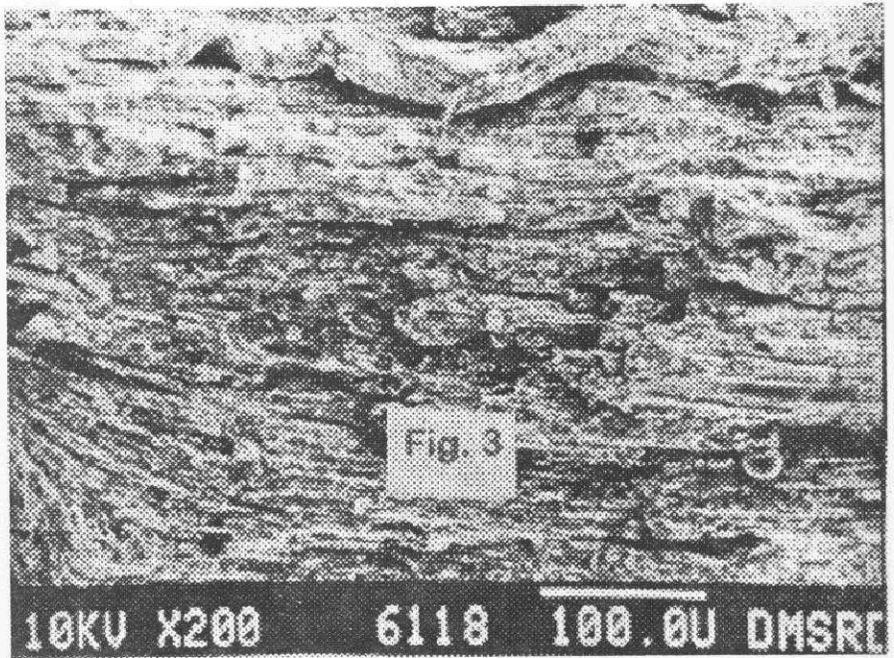
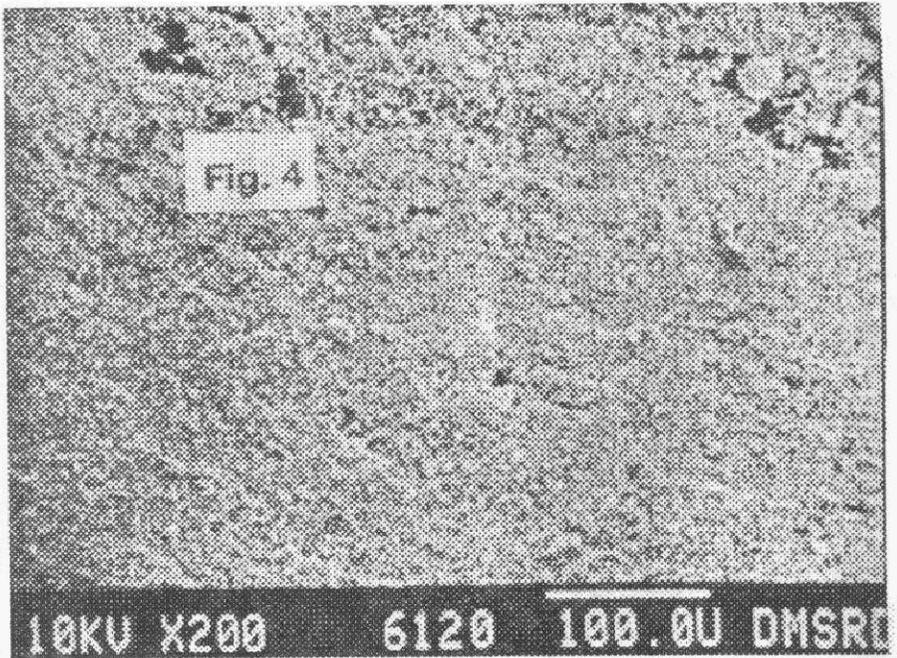Fig. 3 - SEM photograph of Phenolic resin filled vulcanizate of mix C.

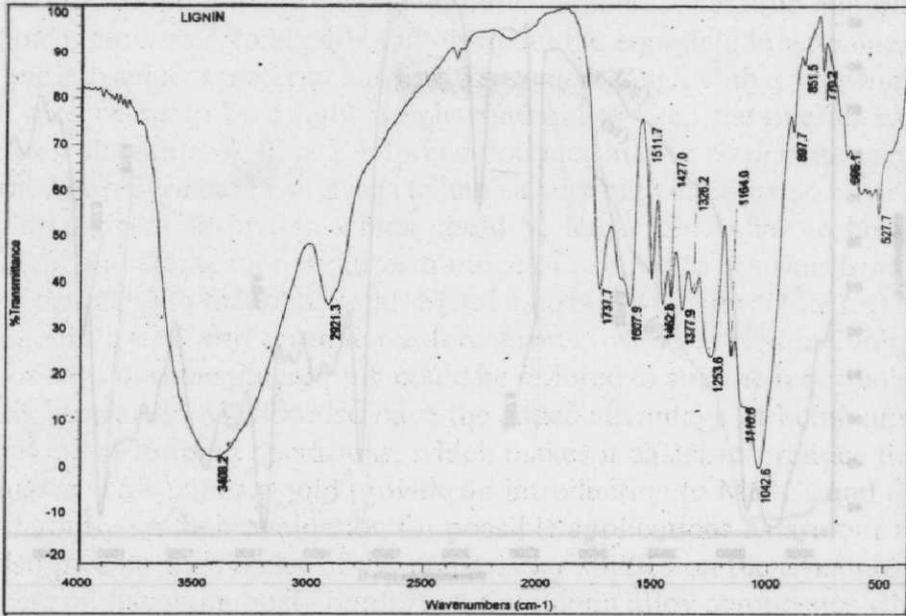Fig. 4 - SEM photograph of Carbon black filled vulcanizate of mix D

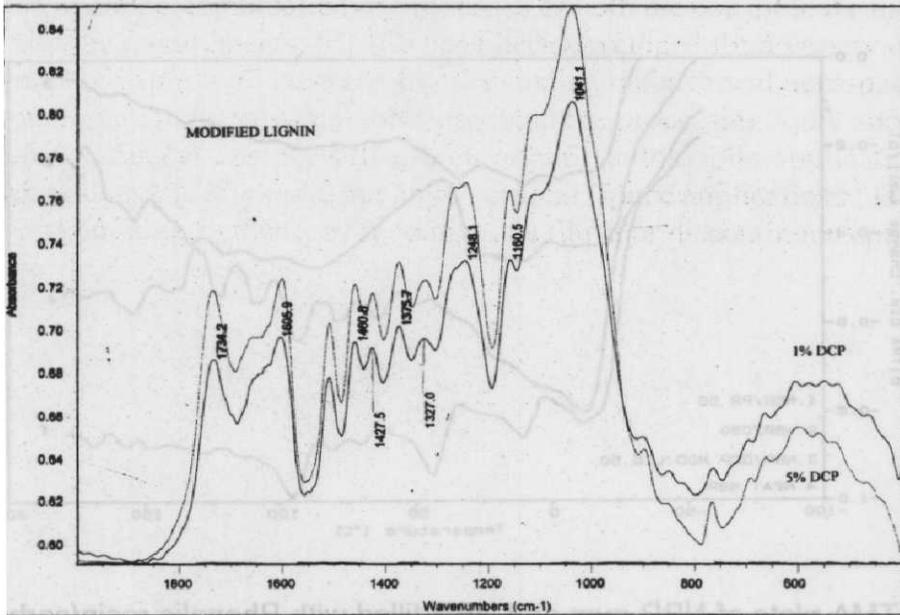Fig. 5 - FTIR spectrum of unmodified Lignin.
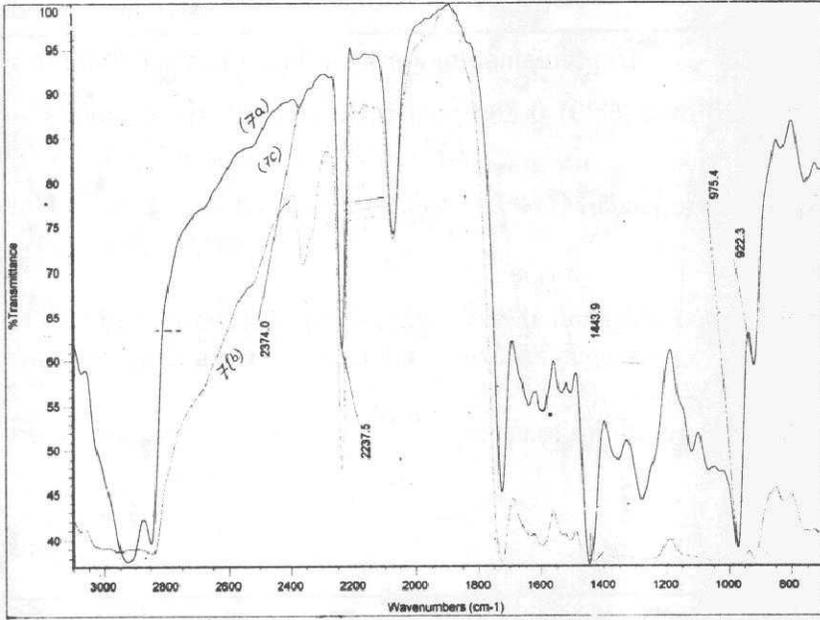

Fig. 6 - FTIR spectrum of DCP modified Lignin.

Fig. 7 - (a) FTIR spectrum of Gum NBR vulcanizate. (b) FTIR spectrum of unmodified Lignin filled vulcanizate. (c) FTIR spectrum of DCP modified Lignin filled vulcanizate.
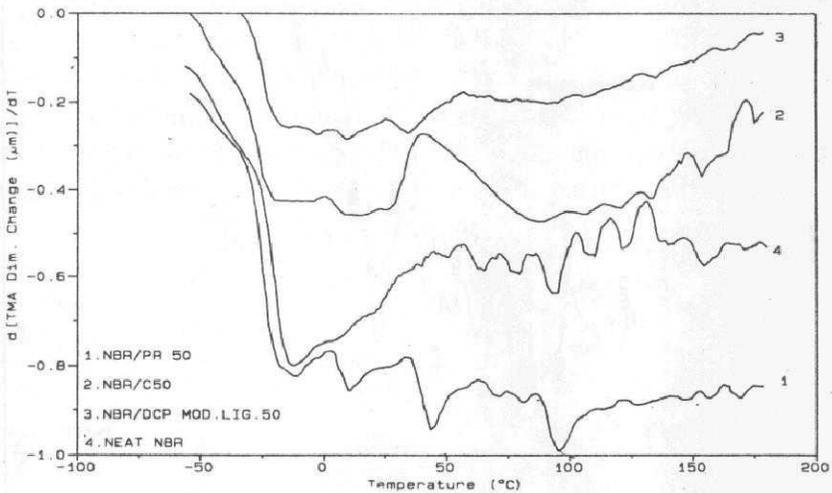

Fig. 8 - TMA plots of NBR gum and NBR filled with Phenolic resin/carbon black/ DCP modified Lignin.
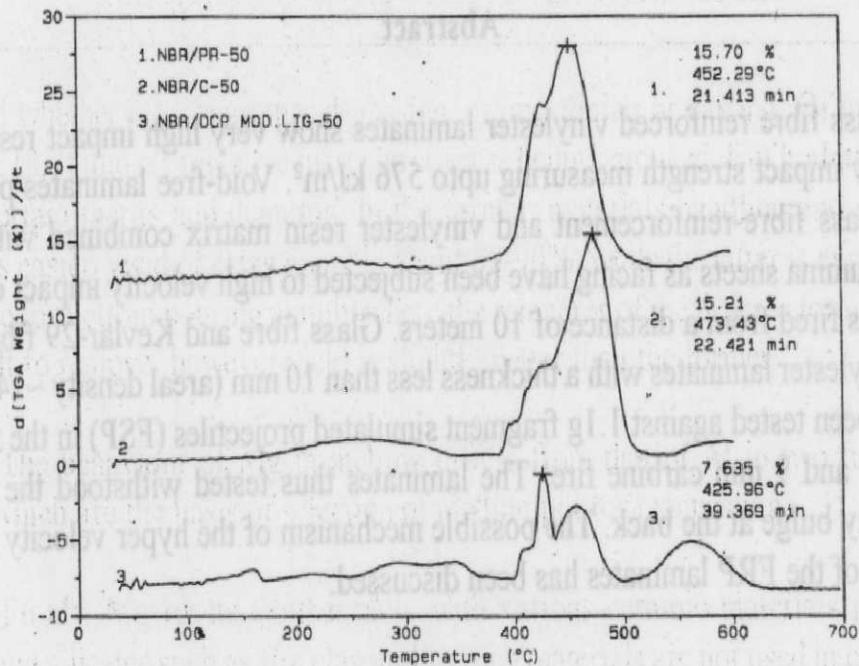
Fig. 9 - TGA plots of NBR filled with DCP modified Lignin, Phenolic resin and
carbon black.