

BUTYL RUBBER-NYLON COMPOSITES WITH IMPROVED FLAME RETARDANCY AND GAS IMPERMEABILITY

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Abstract

Butyl rubber, because of its high packing density and chemical structure is inherently impermeable to air and gases. However, the elastomer is highly flammable owing to its neat carbon-hydrogen backbone structure. The particular rubber is extensively being used as coating materials for nylon, cotton, polyester etc., for development of clothing outfits for service personnel working in hazardous chemical environments. It is, therefore, essential to evolve flame retardant butyl rubber compositions which could make such clothings impermeable to chemical agents having adequate flame retardancy.

The present paper describes an attempt towards using various chemical additives viz. brominated phenyl ethers, chlorinated paraffin, various inorganic oxides and halogenated elastomer, either singly or in combinations as potential flame retardants in bromo-butyl rubber compositions. The cements were then prepared by adding toluene to these compositions (20 to 30% solid content). The homogenised cements were then applied on both sides of nylon fabric with varying add-on concentrations in a laboratory coating machine with doctors blade specially designed for this purpose.

The coated fabrics were cured at different temperatures in step curing between 70-150°C, tested for impermeability against hazardous warfare agents and found to offer enhanced protection against these chemicals. Standard test methods e.g. (a) exposure of the fabric to direct flame as per BS method 3119 (b) limited oxygen index as per ASTM specification D-2663 were followed in the evaluation of flame retardancy. The fabrics showed no after glow, low after flame (2.5 sec. against 6 sec. specified) and 7.2 cm char length against 12 cm max. permissible value. The physicommechanical properties e.g., breaking and tensile strengths were determined. Morphology and rubber fabric adhesion were studied using Scanning Electron Microscopy.

Introduction

A major short-coming of rubber is its burning properties. The flammability of rubber products has for many years been a matter of concern in number of applications, such as cable sheathing, conveyor belt, proof coatings and ventilation duct in mining operation. The research on this subject has lagged considerably behind the corresponding efforts spent in the plastics [1,2]. The flammability of rubber is higher than that of wood or natural fibres. The calorific value of common rubber is between 37000-460000 kJ/kg, whereas that of wood is around 19000 kJ/kg. In addition to this, combustion of some rubbery materials is accompanied by the smoke and soot formation, droplets, and evolution of highly toxic products. Flame retardancy in coating can be obtained by blending the inherently flame retardant elastomers like chlorinated polyethylene (CPE) polychloroprene (PCR), chlorosulphonated polyethylene (CSPE), flame retardant additives or by the combination of these materials.

Opulstil [3] has described a polychloroprene compound with hydrated alumina, antimony trioxide, zinc borate and tricresyl phosphate (TCP), which gives self extinguishing characteristics to the material. Brikenhead [4] has discussed the use of chlorinated elastomers for use in fire retardant surface coatings. Thorpe [5] has prepared copolymers based on a polymerisable material having aliphatic carbon-carbon unsaturation with butadiene polymer and a polyhalogenated cyclopentadiene. The polymer prepared by this method are fire retardant and useful for coatings. It is mentioned in the literature that the use of antimony trioxide and zinc borate in a polychloroprene rubber gives fire resistant coating composition for cloths. The flammability of these coating compositions are in some way related to the concentration of the combustible material (i.e. total concentration of carbon and hydrogen), the amount of HCl and HBr which could be evolved from the vulcanizate, amount of acid acceptor and generation of CO₂ and H₂O from appropriate fillers. Fluorinated elastomers containing more than 60% fluorine by weight, have been claimed to render flammable fabrics self extinguishing.

The present paper describes an attempt to impart flame retardancy in bromobutyl rubber compositions. Seven butyl rubber compounds were made and studied for their physical properties, filler distribution/dispersion and particle size using SEM, thermogravimetric and dynamic mechanical properties, flammability characteristics as well as impermeability against liquid chemical toxicant. In order to ascertain processing of the cement on the nylon fabric, the rheological and cure characteristics of these compositions have been evaluated using Rubber Process Analyzer (RPA-2000). The cement made out of the best formulation, on the basis of above properties, was used to coat nylon fabric in a laboratory coating machine and also tested for specific end use requirements.

Experimental

Compounding

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.

Physical Properties

Developed mixes were vulcanized for 30 min at 150°C and 200 kg/cm² pressure in a hydraulic press having electrically heated platens. Specimen for tensile test were punched out along the grain direction from the vulcanized sheets. Tensile testing was done as per ASTM method D 412-51T, using dumbbell specimens. This test enables to obtain elongation at break and modulus values of the vulcanizates.

SEM Studies

Filler distribution, dispersion and agglomerate size of vulcanizate and failure mechanism have been studied by SEM (model JEOL 35CF). The fractured surfaces of the tensile test specimen were cut carefully without touching the surface. These specimens were stored in a dessicator to avoid contamination from dust particles and then sputter coated with gold within 24h of testing.

Flammability Test

Flammability of all the vulcanizates were tested for vertical flammability and Limited Oxygen Index (LOI) as per BS 3119 and ASTM-D-2863/77 respectively. In vertical flammability test, a test specimen of size (50.8mm x 300mm) and thickness upto 1.2mm is exposed to open flame for 10 sec, the flame was then removed and flammability characteristics of the materials were determined as follows.

- (a) After Flame : The length of time for which the material continues to flame after the ignition, when the source has been removed.
- (b) After Glow : Combustion of material without flame but with the emission of light from the combustion zone. After glow is the time for which the material continues to glow after cessation of flaming or removal of the ignition source.
- (c) Char Length : The maximum extent of damage/charred material is measured in the vertical direction. This parameter indicates the maximum extent of total damage of material ignoring any surface effect such as scorching or smoke deposition.

In LOI test, test specimen is allowed to burn in minimum concentration of O_2 : N_2 that will just support flaming combustion. This is most useful flammability test since it allows one to precisely rate the material on the numerical basis.

Thermogravimetric Analysis

Thermal properties of the vulcanizates were evaluated in a model 2100 (Du Pont, USA) thermogravimetric analyzer at $20^\circ C/min$ heating rate and in nitrogen atmosphere of $60 ml/min$ flow rate.

Impermeability Test

For determining the impermeability, three specimens of rubber sheet/coated fabrics were contaminated with specified quantity of liquid toxicant on a detection paper of $[5 mm \times 5 mm]$ in a petridish. The impermeable material covers the detection paper completely and is sealed with wax on the the petridish. The bottom side of the detection paper can be watched via a mirror because the petridish is situated on the glass plate. A second petridish on top of the test specimen prevents the evaporation of the toxicant. The penetration of the liquid toxicant used gives blue dots on detection paper. The time required to appear blue dot on detection paper is recorded.

Processing characteristics

A small piece of rubber compound sample (approx. 5-7gm) was taken and placed in between dies of the RPA-2000 and the rubber sample was subjected to test configurations e.g., $150^\circ C$ for cure with frequency 100 cycles/min and 0.5° strain. DMSRDE, Kanpur is the only institution in India, where RPA-2000 facility exists. Minimum torque, maximum torque, scorch safety of raw rubber and dynamic mechanical properties of vulcanized rubber were determined on the same sample.

Coating of Cement

Optimized rubber formulation was made into cement by dissolving it in toluene to get dow of 30-40% solid content. Coating of the cement was done in the laboratory coating machine equipped with doctor's blade to adjust various thickness/add-on concentration onto nylon fabric. Figure 1 shows the schematic diagram of the coating machine.

Results And Discussion

Physical properties of the mixes are given in Table 2. Tensile strength, modulus at different elongations and elongation at break value for gum butyl-rubber (mix no.1) are poor and these properties showed hardly any improvement due to addition of

different additives e.g. antimony-trioxide alone in varied concentrations (mix nos. 2&3) or in combination with decabromo-diphenyl ether. This is due to non-reinforcing characteristics of these additives. Addition of chloro-rubber in mix no. 4 showed fall in mechanical properties due to immiscibility between IIR and CLR, which caused improper filler distribution. Addition of tricresylphosphate (TCP) enhanced plasticization and filler distribution as a result of which marginal improvement in tensile strength and elongation at break values took place. However, the addition of polychloroprene in combination with CLPE and MgO (mix no. 7) resulted marked improvement in physical properties due to compatibilization of IIR and PCR in presence of CLPE. All these resulted in finer phase morphology, homogeneous distribution of filler particles with reduced scale of dimension and significant improvement in the tensile strength and modulus values.

SEM observations closely resemble physico-mechanical properties. In case of mix no. 4 the addition of chloro-rubber resulted in coarse phase morphology, poor filler-matrix adhesion as well as larger filler agglomerates which were pulled out from the matrix phase (Figs.2 A&B). Physical properties are, therefore, impaired compared to mix no. 1 as mentioned earlier. In the case of TCP addition, as in mix no. 6, finer distribution of filler particles in the matrix are evident (Fig.3). However, compatibilization of IIR&CR in presence of CLPE, resulted in much smoother morphology coupled with finer dispersed particles as low as 4 micron and absence of any dewetting or artifacts (Fig. 4).

The flammability of the mixes was evaluated by (a) determination of LOI (Table 3) and (b) direct exposure to flame as per British standard (Table 4). In LOI evaluation it has been observed that addition of Sb_2O_3 alone cannot generate any significant improvement in flame retardancy. The improved LOI values by the addition of chloro-rubber, saytex, or saytex and TCP are probably due to presence of halogen containing additives which liberate HCl and oxide of phosphorus thereby inhibiting flammability. However, presence of acid acceptor as well as increased molar percentage of chlorine further by addition of PCR resulted in marked improvement in flame retardancy. Fig. 5 shows the plots of variation of LOI with respect to particle size of filler agglomerate and mole % halogen and phosphorus containing additives in mixes. In case of mix no. 7 both lowest filler particles as well as maximum mole % halogen containing additives resulted in maximum LOI for the mix compared to others. In a comparatively more stringent flammability test as per British standard which closely simulates actual field conditions, only composition no. 7, was found to sustain a direct exposure to naked flaming (Table 4) and offered some meaningful results. Enhanced thermal stability of mix no. 7 was also observed in TGA analysis, Fig. 6 shows the plots of derivative weight loss of the composition with respect to temperature and is also compared to that of mix no.1 not only the main decomposition peak is shifted to 428.5°C from 409°C of that compound no.1 but TGA plot of mix no.7 also

shows appearance of separate peak maxima at 313°C. Decomposition of flame retardant additives prior to actual degradation of bare polymer protects the matrix as well as form a grid or barrier of inflammable sheath on top of the matrix. Lower percentage of material loss (54.2%) compared to base matrix (92%) at final decomposition point was also evident in support of our conclusion.

Based on above observations, compound no.7 was chosen for further studies. Impermeability of vulcanized rubber sheet of varied thickness towards a chemical liquid toxicant was measured and these results are depicted in Table-5. Passage of liquid molecule through rubber phase is a kinetic/transport phenomenon, and at a particular temperature the rate depends on both thickness, matrix rigidity/compactness as well as nature and size of distributed filler. As expected, increasing thickness increased the break through time. Presence of filler also deviate the flow path of the liquid and registers hindrance to flow of the same through a solid phase. Relatively higher break through time (BTT) value at much lower composite thickness was probably due to formation of a compatible and homogenous phase morphology.

Processing characteristic during curing of mixes 1 and 7 were determined by RPA and results are tabulated in Table 6. Scorch safety for the unfilled mix no.1 was very good, the same was not found to deteriorate much even with the addition of flame retardant additives due to their acidic nature and heat stability as depicted in TGA study mentioned earlier. Subsequent to onset of curing the mix no.1 showed much steeper torque development compared to mix no.7, which showed a moderate torque increment of marching variety. This accounted for higher heat stability of mix no.7 compared to mix no.1. However, both the maximum torque and the optimum cure time had not varied significantly due to addition of flame retardants in mix no.7. This justifies the modified cure cycle in both cases. Broader hump in the Tan δ plot of the unfilled compound compared to mix no. 7 (Fig.7), resulted due to restricted plasticity and mould flow of unfilled compound. Addition of fillers not only reduce the nerve of the stock but also resulted attainment of steady Tan δ value at a faster spell.

The rubber cement with composition no.7 was prepared by adding toluene to obtain dow/cement of 30-40% solid content. Homogenized cement was applied on both sides of the nylon fabric with varying add-on concentration and evaluated for end use properties e.g. flame retardancy and permeability against liquid chemical toxicant. BTT results of the coated fabric both prepared as above as well as obtained from trade are given in Table 7. Minimum requirement of 6h BTT not available in trade was obtained at 0.75mm thickness of rubber coating. The coated fabric was also subjected to exposure of direct flame test and showed no after glow, low after flame (25s against 6s specified) and 7.2cm char length (12cm maximum).

Conclusions

1. Halogen and phosphorus containing additives in association with acid acceptor are found to be more effective than inorganic oxide in the improvement of inflammability of butyl rubber.
2. Uniform distribution of filler with lowest particle size as well as compact matrix without any flaw or microheterogeneity offer enhanced impermeability.
3. Taking in consideration of above variables suitable butyl rubber compositions can be coated onto nylon and may be utilized for developing clothing outfits for defence personnel working in hazardous chemical environments.

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Table 1
Composition of Mixes

Sl. No.	Ingredients	1	2	3	4	5	6	7
1	Butyl rubber	100	100	100	100	100	100	100
2	Polychloroprene	—	—	—	—	—	—	20
3	Chloro Rubber	—	—	—	20	—	—	—
4	Chlorinated Paraffin wax	5	5	5	5	5	—	5
5	Stearic Acid	1	1	1	1	1	1	1
6	TCP	—	—	—	—	—	5	—
7	PBNA	1	1	1	1	1	1	1
8	ZnO	10	10	10	10	10	10	10
9	Sb ₂ O ₃	—	10	20	10	10	10	10
10	Saytax	—	—	—	—	20	20	20
11	CLPE	—	—	—	—	—	—	5
12	MgO	—	—	—	—	—	—	4
13	Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
14	TMTD	1.5	1.5	1.5	1.5	1.5	1.5	1.5
15	MBTS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
16	ZDC	0.5	0.5	0.5	0.5	0.5	0.5	0.5

1 Butyl Rubber - Bromobutyl rubber (BIIR-2244 Ploysar, USA)

2 Polychloroprene - Neoprene WMI grade DU PONT, USA

3 Chloro Rubber - 36% chlorine content

4 Chlorinated Paraffin wax - 58% chlorine content

5 TCP - Tricresylphosphate

6 PBNA - Phenyl betanaphthyl amine

7 Saytax - Decabromo-diphenyl-ether (Saytex)

8 CLPE - Chlorinated polyethylene 0136 Tyrin DOW Chemical, USA

9 TMTD - Tetramethyl thiuram disulphide

10 MBTS - Mercapto Benzothiazole sulphide

11 ZDC - Zinc diethyl dithiocarbamate

All the chemicals were provided by Bengal Water Proof, Calcutta

Table 2
Physical Properties of Vulcanizates

Property	1	2	3	4	5	6	7
Tensile Strength, kg/cm ²	35	35	41	26	42	48	92
Modulus at 400% elongation, kg/cm ²	13	15	17	—	16	7	28
Modulus at 500% elongation, kg/cm ²	18	22	23	—	22	13	36
Elongation at break, %	825	850	750	700	800	920	850

Table 3
Limiting oxygen index (LOI) of rubber vulcanizates

Compound Number	LOI	Specified Limit
1	16.5	25 minimum
2	17.0	-do-
3	17.5	-do-
4	18.2	-do-
5	20.0	-do-
6	20.4	-do-
7	25.0	-do-

Table 4
Flame retardancy of rubber vulcanizates
(As per BS 3119)

Compound Number	After flame (in sec)	After Glow	Char length (in cm)
1-6	Burnt completely	-	-
7	2	Nil	7.2

Table 5
Break Through Time (BTT) test result of vulcanizate number 7

Thickness of rubber sheet, (mm)	Break Through Time (in hour)
0.55	3.00
0.62	4.15
0.75	More than 6
0.80	More than 6
0.95	More than 6

Table 6
Processing Characteristics

Parameters	Compound Number 1	Compound Number 7
Minimum torque, kg-cm	0.87	1.08
Maximum Torque, kg-cm	3.97	3.62
TS1 (Scorch safety), minimum	4.84	3.32
T10 minimum	3.56	1.93
T90 (curing time) minimum	8.49	7.40

Table 7
BTT results on coated fabric of vulcanizate number 7

Thickness of rubber coating, mm	Type of sample	BTT, h
0.60	Trade	2.40
0.62	Trade	4.15
0.01	Experimental	1.22
0.20	Experimental	4.00
0.75	Experimental	More than 6

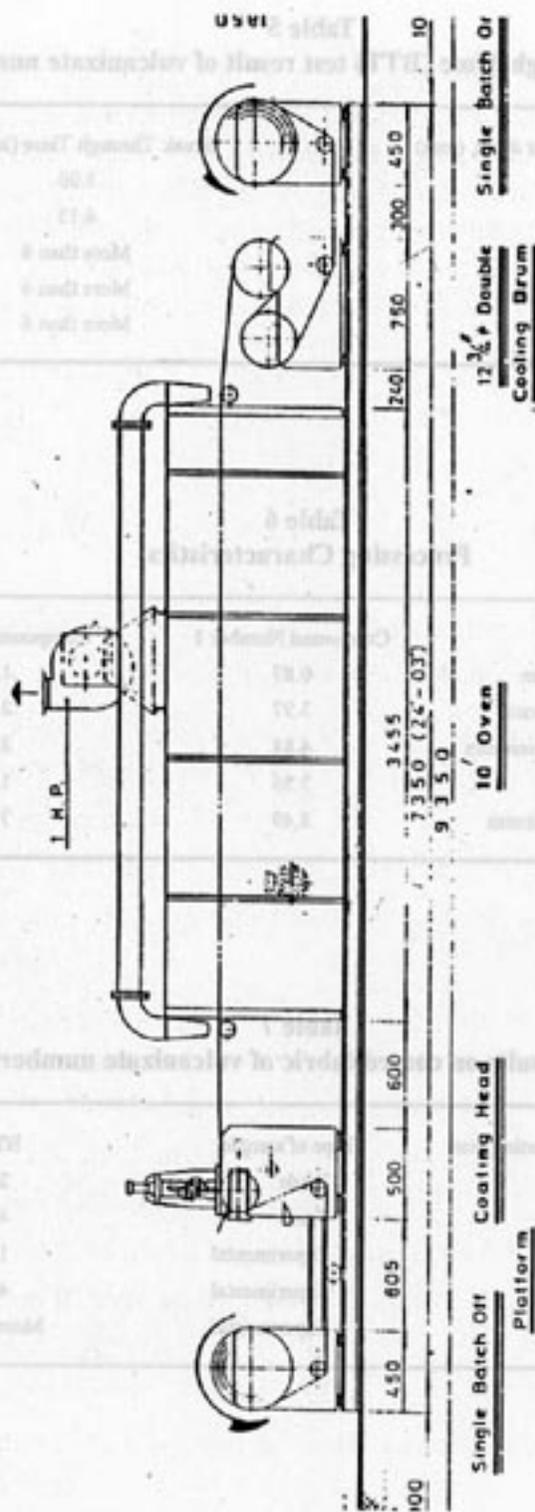


Fig. 1 - Schematic diagram of the coating machine.

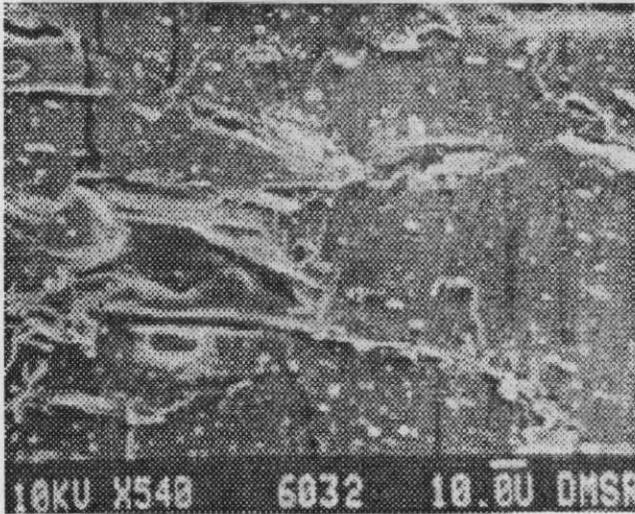


Fig. 2A - SEM photograph of cross section of the vulcanizate containing chlororubber (mix No. 4) showing improper filler distribution, grooves and artifacts.

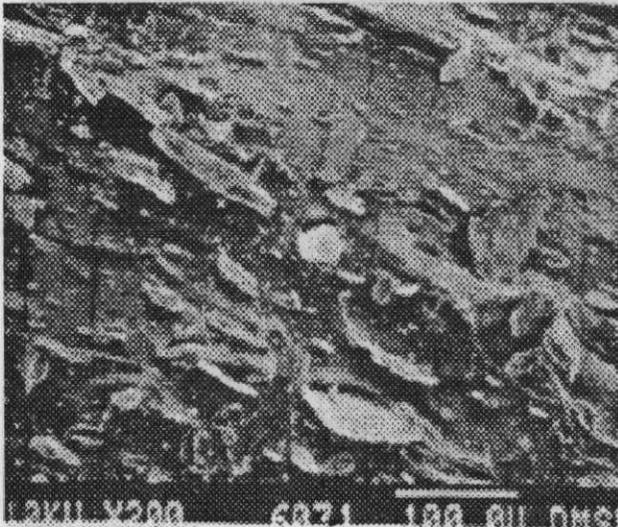


Fig. 2B - SEM photograph of cross section of mix No. 4 in higher magnification.

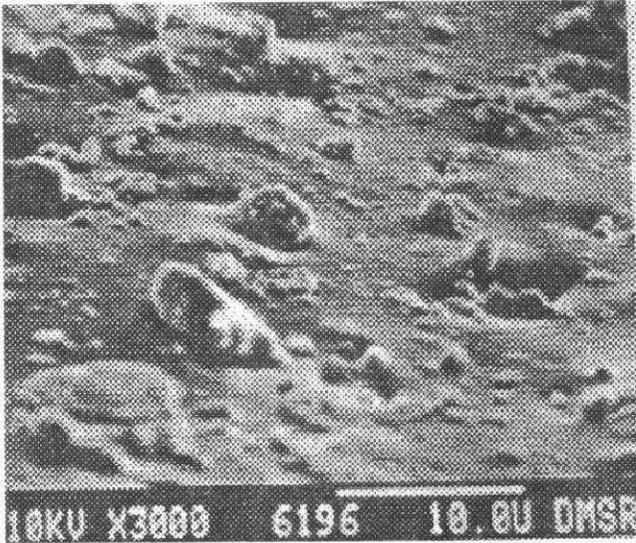


Fig. 3 - SEM photograph of mix No. 6 containing TCP showing finer phase morphology compared to mix No. 4.

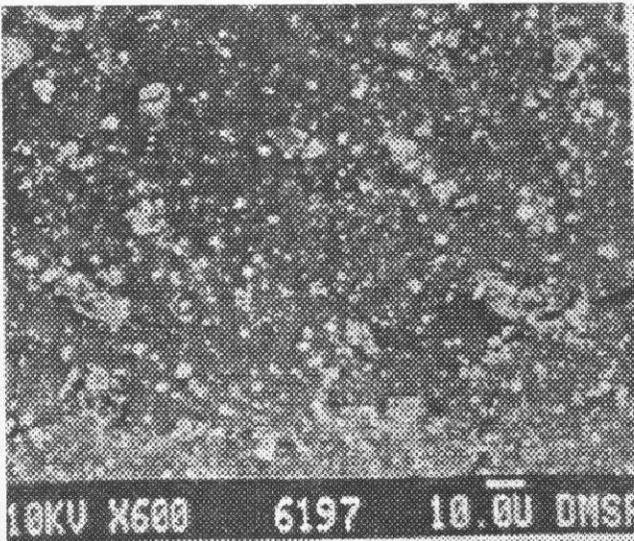


Fig. 4 - SEM photograph of mix No. 7 of IIR/CR blend added, with CLPE, showing finest filler distribution/size and absence of dewetting.

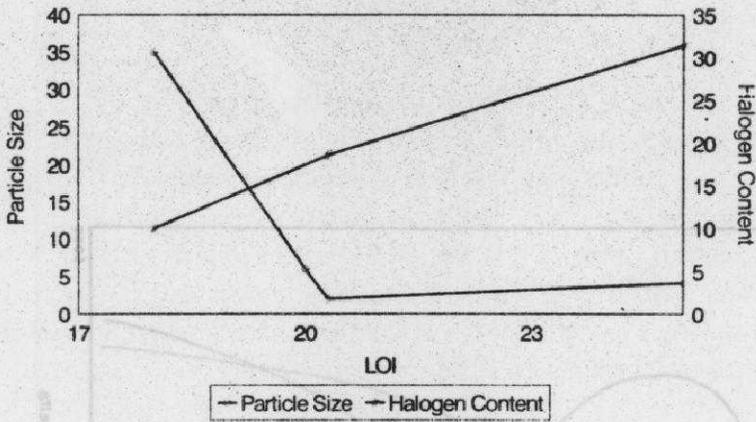


Fig. 5 - Variation of LOI (Limiting Oxygen Index) with respect to particle size and halogen content.

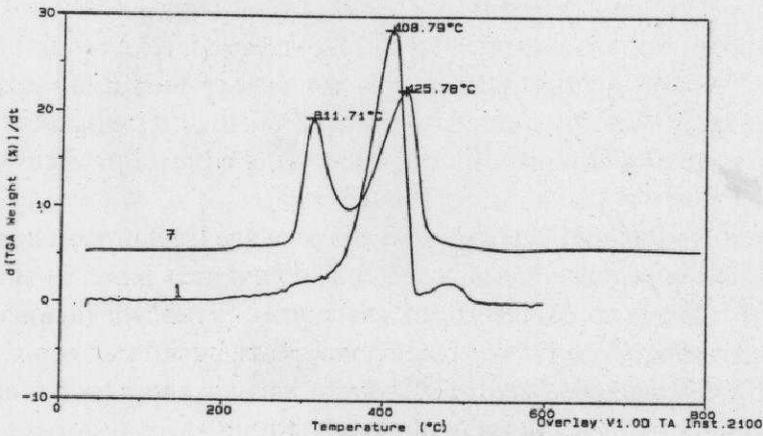


Fig. 6 - TGA derivative plot of mix No. 1 & 7 showing different degradation peaks and percentage weight loss.

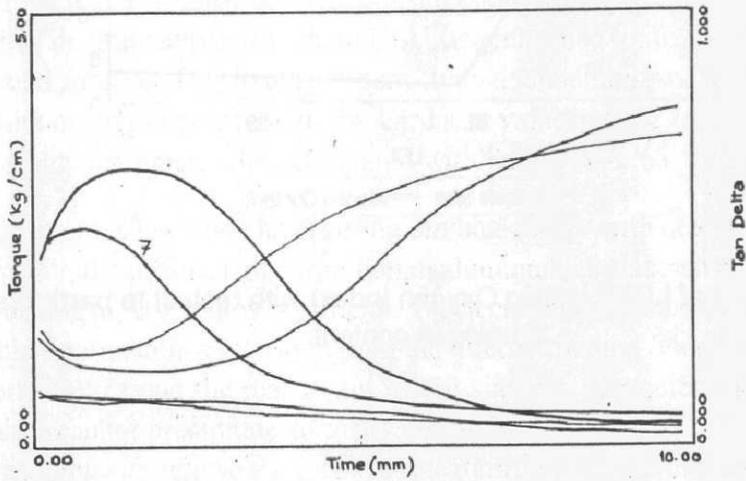


Fig. 7 - RPA-2000 cure curve showing the difference in the curing characteristics of mix No. 1 & 7.