Effect of Fillers and Fire Retardant Compounds on Hydroxy-Terminated Polybutadiene-Based Insulators

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ABSTRACT

A series of polyurethane compositions have been formulated using hydroxy-terminated polybutadiene as polymeric binder and carbon black as a major filler. Various binder-to-filler ratios of the formulations were evaluated to get calendered sheets. The formulations have been characterised for pot-life and rollability and the calendered sheets for mechanical and thermal properties, burn rate, glass transition temperature, shore hardness and density. The different fillers tried were varieties of carbon black as a major filler; metal oxides, silicates and organic compounds; and fire retardants, such as zinc borate, sodium metaborate, ammonium dihydrogen phosphate and antimony trioxide. The structure and morphology of the fillers have been correlated with the properties. The optimised composition has been evaluated in an end-burning motor, as an insulator for case-bonded application, using a typical composite propellant. The results of interface bonding between the propellant and the insulator have also been presented.

Keywords: Composite propellants, HTPB-based insulators, propellant binders/fillers, HTPB-based polyurethanes, hydroxy-terminated polybutadiene binders, case-bonded technology

1. INTRODUCTION

Hydroxy-terminated polybutadiene (HTPB) is the workhorse binder used for processing of composite propellants. HTPB can be crosslinked with chain extension by reaction of the terminal hydroxyl groups with a variety of isocyanates to yield vulcanisates comparable to those obtained from conventional butadiene rubbers[1].

The liquid nature of HTPB allows easy reaction with isocyanates even at ambient temperature and properties of elastomers produced can easily be improved either by chemical modification of the polymer backbone or by the addition of reinforcing fillers, such as carbon black. HTPB-based polyurethanes have superior hydrolytic stability and the mechanical strength is generally lower than that of their polyester or polyether analogues.

The use of HTPB-based polyurethanes as an insulator, liner or inhibitor for rocket propellants has not been studied exhaustively. Most of the work is restricted to liner coatings only. Maucourt[2] describes HTPB/isophorone di-isocyanate (IPDI)-based polyurethanes composition for coating the inner surface of a propulsion unit. This has been used for a butalane propellant by spraying

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di-isocyanate (DDI), carbon black as a filler and an aziridine-based bonding agent has been used. This mixture was coated on an ethylene propylene diene monomer (EPDM) insulator, and it has been claimed that the liner system developed prevents plasticiser migration from propellant to insulator. Probster[4] also reports liner composition based on HTPB-isodecyl pelargonate (IDP) hexamethylene di-isocyanate (HDI) and oxamide for rocket motors insulated by EPDM or terpolymer of butadiene, acrylic acid and acrylonitrile (PBAN) rubbers. Hemminger[5], Wrightson[6,7] and Pierce[8] have also reported HTPB-based composition for lining the rocket motors.

At present, nitrile rubber-based composition, specially developed as an insulator is being used for insulating the rocket motors for space applications, but no information is available in literature about shelf-life of these insulators. In view of various advantages offered by HTPB-based polyurethanes, a study was undertaken to use these compositions as an insulator for case-bonded technology. The bonding properties are expected to be good as the basic matrix (of HTPB) for propellant, insulator and liner remains the same. The chemical resistance and weathering properties of polyurethanes are far superior as compared to nitrile rubber[9].

Curing of HTPB uses urethane reaction which is quantitative in nature and progresses to completion at a convenient rate, giving good and repeatable mechanical properties. The urethane linkage formed is very stable.The required mechanical properties can be achieved by suitably tailoring the polymer binder using di-functional/tri-functional crosslinking agents and different curatives, fillers, plasticisers, etc. The effect of fillers on reinforcement and fire retardancy of these polyurethane compositions has been reported.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

HTPB, molecular weight ($\overline{Mn}$) 2200–3000, –OH value (40 mg–50 mg) of KOH/g was used as a 98 per cent) has been used as a curative; 1,2,6-hexanetriol (HT) (purity > 98 per cent) has been used as a crosslinking agent.

Carbon black, of three different varieties, N-774, N-550 and N-330, was used as a major filler. Ten different fillers, such as antimony trioxide, melamine, lithopone, asbestos, titanium oxide, silica, kaolin, mica, talc, alumina trihydrate (commercial grade) have been used as fillers (8 per cent) along with zinc borate, sodium metaborate, ammonium dihydrogen phosphate as fire retardant compounds. Particle size range for all the fillers used was between 2μ and 10 μ.

2.2 Characterisation

The polyurethane matrix was characterised for mechanical, thermal and spectral properties. Tensile properties have been tested according to ASTM:D-638 using Instron-1185, tensile testing machine. Shore hardness A was measured using Shore hardness tester model SHR-4,111.

Differential thermal analysis (DTA) studies have been carried out using indigeneously fabricated micro DTA with a heating rate of 10 °C/min in air. Glass transition temperature (T_g) has been determined by differential scanning calorimetry (Mettler DSC-30 machine). Thermal conductivity was measured by thermal conductivity tester model TCHM-DV (R/D Co., USA). Relative rate of burning was measured using ASTM:D-635 (flammability).

2.3 Preparation of Polyurethane Sheets

All the solid ingredients were dried in air oven at 100 °C for a minimum of 6 hr and binder material was deaerated under vacuum (< 10 mm Hg). Moisture level for all ingredients as determined by Karl Fischer reagent was below 0.1 per cent.

The binder-to-filler ratio of 50:50 gave a rollable dough of polyurethane matrix and hence this ratio has been maintained throughout the experimentation. The binder, filler and additives were mixed in a sigma blade mixer following a particular sequence of addition. After complete

grade	(nm)	(kgf/cm^2)		
N-774	61-100	48	99	1.21
N-550	40-48	57	114	1.22
N-330	26-30	60	107	1.22

rolling trials using small amount of dough after a fixed interval of 30 min at ambient temperature. (Initially, the dough sticks to the rollers and there is no sheet formation, indicating that the dough has not sufficiently cured for subjecting it to calendering operation. A tacky stage comes when the dough does not stick to the rollers and a sheet of uniform thickness can be calendered. If the elapsed time exceeds the pot-life, sheet formation becomes difficult and a cured powdery hard mass is formed).

The dough was calendered into sheets of 2.5 mm to 3.0 mm thickness using two-roll mill. The relative humidity during the mixing and rolling was maintained at 55 ± 5 per cent. The calendered sheets were sealed in polythene bags for further characterisation.

3. RESULTS & DISCUSSION

In an elastomer matrix being developed for propellant applications, fillers are mainly used for reinforcement as well as for fire retardancy. In the present study, carbon black of three varieties was used as a major filler and the effect of particle size on mechanical properties and processing has been discussed. The results obtained are presented in Table 1.

Carbon black is the finely divided group of materials and is available commercially in various particle sizes and structures. The X-ray diffraction pattern indicates that carbon black consists of well-developed graphite platelets stacked roughly parallel to one another but random in orientation wrt adjacent layers. This arrangement is termed as hexagonal turbostratic[10].

The tensile strength increases as the particle size of carbon black decreases from N-774 to N-330. This clearly indicates the reinforcing effect of carbon black with decrease in particle size. Carbon black is an outstanding reinforcing filler for both natural and synthetic rubber. Although the mechanism of reinforcement is not completely understood, it appears to add a network of many relatively weak fix points to the more diffuse network of strong primary bond cross-links introduced by curing or vulcanisation. Curing or vulcanisation restricts the long range movements of the polymer molecule but leaves their local segmental mobility high. Reinforcement stiffens the mass and improves its toughness by restricting this local freedom of movement. The three parameters, viz., particle size, p*H* and structure index appear to determine the reinforcing behaviour of carbon black.

It was observed that properties like tensile strength, abrasion and tear resistance, hardness and toughness increase with decreasing particle size[11]. The present observations are in agreement with the reported one. However, the processibility becomes poorer as the particle size decreases. The reported evidence for reinforcement of carbon black points to the existence of chemical bonds or chemisorptive linkages than only physical adsorption[12]. It is reported that carbon black surfaces contain functional groups capable of reacting with polymer molecules to form grafts during processing and vulcanisation[13]. Further, numerous reactions of hydrocarbon polymers with carbon black have been demonstrated. In fact, several possible mechanisms exist by which grafts may be formed, e.g. carbon black chemisorb olefins at vulcanisation temperature[14].

Taking into consideration the extent of reinforcement and ease of processing, the N-550 variety of carbon black was selected for further studies. Part of carbon black (8 per cent) was replaced by 10 different fillers from different chemical classes. Antimony trioxide, TiO_2, lithopone, silica and $Al_2O_3.3H_2O$ are oxides; kaolin, mica, talc and asbestos are silicates; whereas melamine is an organic filler. The polyurethane sheets so obtained were characterised and the

Sb_2O_3	49.8	139	0.47	1.24	65-67	480	520	0.101
Lithopone	53.8	143	0.58	1.24	64-65	505	580	0.108
Melamine	49.0	142	0.63	1.21	64-66	480	495	0.105
Asbestos	53.6	140	0.44	1.23	66-67	490	600	0.108
TiO_2	50.2	109	0.61	1.22	63-65	500	600	0.112
Silica	53.4	106	0.58	1.22	68-69	500	570	0.108
Kaolin	53.0	141	0.66	1.23	65-66	510	600	0.115
Mica	51.1	126	0.66	1.22	65-66	500	590	0.119
Talc	52.3	145	0.56	1.22	63-65	510	530	0.138
Al_2O_3	43.7	131	0.52	1.23	63-66	505	605	0.151

Composition : Binder + Filler (Tackifier + Carbon black + Filler : 4 + 40 + 8)

results are presented in Table 2. The reinforcement in mechanical properties is comparatively better for lithopone, asbestos, silica, kaolin and talc than for antimony trioxide, melamine, TiO_2, mica and $Al_2O_3.3H_2O$.

Asbestos is a well-known fibrous reinforcing filler, while kaolin is a two-layered hydrous alumino silicate consisting of chemically bonded layers of silica and gibbsite (hydrous alumina) and has the form of hexagonal platelets. Finer particles are thin plates. This typical form of kaolin is responsible for the reinforcement, improved bonding with polymers, ease of dispersion, better flow and non-reactivity in critical applications[15]. Talc is a hydrated magnesium silicate (3 MgO, 4SiO_2, H_2O) and the finely ground product consists of thin plalelets and due to this platy nature, it is considered to be a reinforcing filler in many plastic applications[16]. The particulate amorphous silica is colloidal and has surface area as much as 380 m^2/g. qualities provide thixotropy, anti-settling, anti-blocking and true reinforcement[17]. Lithopone also gave reinforcement.

In case of fillers like $Al_2O_3.3H_2O$ and TiO_2, the tensile properties were found slightly on the lower side because of the poor wettability of the particles by the polyurethane matrix.

The burn rates of the cured sheets containing asbestos, Sb_2O_3, and $Al_2O_3.3H_2O$ were lower than the remaining fillers. This may be due to the fact that the inorganic oxides are non-combustible and provide fire resistance to filled polymers by reducing the volume of combustible matter in the filled composition, and hence may serve as fire retardant fillers for insulator compositions, provided they meet the requirement of low densities. Fillers, such as alumina trihydrate increase fire resistance by liberating non-combustible gases when they are heated. These gases withdraw heat and can also reduce the oxygen concentration of the air surrounding the composition[18].

Asbestos is a hydrated magnesium silicate $Mg_6[(OH)_4\,Si_2O_5]_2$ and has high heat resistance and ability to produce low density product and is commonly used as reinforcing filler[19] for insulation compositions.

The density of the filled polyurethane sheets lies between 1.20 g/cm^3 and 1.24 g/cm^3, depending upon the density of the individual filler. The lower values are preferable to reduce the inert mass of the rocket motor.

The Shore A values are almost the same for all the additives. The resistance of a fabricated rubber article to indentation, its hardness is influenced by the amount and shape of its particles. Fillers in the form of platelets or flakes, such as clays impart greater hardness to elastomers than other shapes at equivalent loadings.

Zinc borate	0.51 (0.38)	37.7 (33.3)	107 (130)	63-64 (60-62)	1.22 (1.21)	505 (510)	605 (630)	0.132 (1.53)
Sodium metaborate	0.45 (0.43)	50.2 (37.7)	126 (157)	62-65 (60-61)	1.23 (1.22)	470 (515)	530 (695)	0.145 (0.142)
Ammonium Dihydrogen phosphate	0.40 (0.40)	33.9 (35.3)	117 (120)	62-63 (60-62)	1.20 (1.22)	505 (505)	665 (680)	0.147 (0.148)
Antimony trioxide	0.54 (0.44)	53.4 (53.6)	105 (140)	68-69 (65-67)	1.22 (1.23)	500 (490)	570 (570)	0.140 (0.135)

Composition : Binder+Filler [Tackifier + Carbon black + Silica (asbestos) + Fire retardant : 4 + 38 + 4 + 4]
Values in brackets are those pertaining to asbcstos additive in place of silica
*Burn rate for polyurethane sheets only with carbon black = 0.80 mm/s

The DTA thermograms of all the compositions showed two distinct exotherms. The first exotherm can be assigned to the thermo-oxidative degradation of the polyurethane linkage. The second exotherm can be assigned to the degradation of rigid polyurethane linkage[20]. As the melting/ decomposition temperatures of all the fillers were very high, the decomposition pattern for individual filler had no appreciable change. The observations of thermal stability are supported by the reported observations of effect of di-isocyanate structure on the relative thermal stability of polyurethane elastomer where a system consisting of polycaprolactone/di-isocyanate/BDO-type elastomer was studied[21].

The T_g by DSC thermogram was –77 °C, showing that the polyurethane rubber has excellent low temperature properties. The T_g of HTPB is – 80 °C. These observations are consistent with findings of Medalia and Datta[22, 23] for rubbers filled with carbon black. The adsorption of polymer segments on the filler surface leads to partial loss of mobility of the chains. As rubbery behaviour of a polymer depends on the ability of its molecules to engage in long range convolutions, any loss of mobility affects the elastomeric properties of the rubber. Studies on proton magnetic resonance in carbon black-reinforced rubbers[24] have shown that there is indeed loss in segmental mobility and maximum restriction in movement is confined to a layer of 5 Å at the surface. The thermal conductivity values show only slight variation, being maximum for $Al_2O_3.3H_2O$.

Fire retardancy is an important parameter for insulating polymers and is achieved by introducing a halogen atom on the polymer chain or by halogen/phosphorus or some minerals in the polymer matrix.

Tables 3 presents the data on burn rate, mechanical and physical properties of HTPB-based polyurethane filled with silica and asbestos along with different fire retardant compounds.

The burn rate for the polyurethane sheet without filler and fire retardant (using only carbon black as a filler) is 0.80 mm/s. The burn rate data shows that ammonium dihydrogen phosphate gives slowest burn rate in both the combinations with silica and asbestos (0.40 mm/s). Ammonium dihydrogen phosphate show improvement in fire retardancy.

All the three fire retardants except Sb_2O_3 adversely affect the mechanical properties. This may be due to poor wettability because of their morphology. Considering the processing and mechanical properties aspects, silica and antimony trioxide combination was selected for application studies. Asbestos was not selected because of its toxicity, hazard and pollution problems.

DTA does not reveal any change, and thermal conductivity values are almost similar for all compositions.

peel-off strength lies in between 1.2 kgf/cm to 2.3 kgf/cm with cohesive failure in propellant which proves excellent bonding. The bond strength between the metal and the insulator was 8 kgf/cm^2 to 10 kgf/cm^2 with a cohesive failure in insulator.

A medium size rocket motor (OD 230 mm, ID 200 mm, L 205 mm) was selected for actual application studies. The motor surface was prepared by acid pickling, sand blasting and solvent cleaning. The sheets of exact dimensions were hand laid using epoxy pre-coat. Firm bond was achieved using inflated balloon technique (pressure 25 psi to 30 psi). The insulator surface was coated with a liner coating of HTPB-TDI composition and a typical composite propellant composition based on HTPB-AP-*Al* was cast in pre-insulated liner coated rocket motor. The propellant was cured, X-rayed and subjected to static evaluation in end-burning mode

The propellant performance was smooth. The pressure level was nearly constant which showed that the bond between propellant-insulator is excellent. Post-firing observations revealed the presence of semi-charred insulator sheets throughout the motor length.

4. CONCLUSION

The filled polyurethane formulation with 50:50 binder-to-filler ratio, using carbon black (N-550) as a major filler with a combination of silica and antimony trioxide as a fire retardant gave desirable processibility, highest mechanical properties, adequate thermal stability, required Shore hardness, low density and low burn rates. The bonding characteristics of these polyurethane-based insulator sheets with propellant as well as metal were excellent. The effectiveness of polyurethane compositions as an insulator for case-bonded motors has been conclusively established by successfully static firing of end-burning motors.

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