Defence Science Journal, Vol. 56, No. 3, July 2006 pp. 309-320

REVIEW PAPER

Ethylene-propylene Diene Rubber as a Futuristic Elastomer for Insulation of Solid Rocket Motors

C.M. Bhuvaneswari, M.S. Sureshkumar, S.D. Kakade, and Manoj Gupta.
High Energy Materials Research Laboratory, Pune-411 021

ABSTRACT

The study carried out so far on the application of ethylene-propylene diene rubber (EPDM) in the field of insulation of case bonded solid rocket motors has been reviewed. The various studies by the authors (unpublished work) have also been reported. All these findings bring out the excellent potential of EPDM as insulator in view of its ageing resistance, low-temperature flexibility, low erosion rate, and low specific gravity.

Keywords: Solid rocket motors, insulation, ethylene-propylene diene rubber, ablation resistance, EPDM, case-bonded solid rocket motors

1. INTRODUCTION

Certain elastomers find use as thermal insulators for case-bonded solid rocket motors (SRMs)[1]. Insulators, by forming the inner lining of rocket motors, prevent their exposure to the extremely high temperature gases of the propellant during combustion and help the integrity of motor without failure during operation. Selection of an insulation system for solid propellant motor applications involves considerations such as design function, material bonding, compounding and fabrication costs, fabrication techniques, storage, handling, environmental exposures, etc[2].

Apart from general requirements like superior thermal resistance etc, the insulator should be lightweight with low thermal conductivity and good mechanical properties. The insulation must remain intact and fully functional throughout propellant combustion and there should be no migration of its components to or from adjacent interfacial surfaces. It should also retain its elastomeric characteristics to avoid brittleness over operational temperature range for required duration of time to avoid catastrophic failure of the entire mission[3].

Nitrile rubbers, PDMS (polydimethyl siloxane), polyisoprene are few of the various elastomers used as insulators in solid rocket motors[4]. Nitrile/rubber[5]-based insulation system is being currently used in Indian space programme. Skolnik[6], *et al*. have reported the efforts made for replacement of nitrile-rubber based insulation by ethylene-propylene diene rubber (EPDM)-based non-asbestos insulation for Tomahawk booster motor.

The technology for the manufacture of case-bonded motors [7-8] and insulation laying of nitrile rubber has been well established. But nitrile rubber-based insulation suffers from the disadvantages such as limited shelf life, higher density, inferior low temperature properties etc. The evaluation of elastomers like EPDM[9-14] to replace nitrile rubber in Indian space and missile programme is in progress.

Revised 10 January 2006

The use of EPDM as an insulator for case-bonded solid rocket motors was evaluated more than a decade ago[15] and found feasible. Being a material with a low specific gravity[16, 17], EPDM has emerged as a novel material for manifold applications including insulation for solid rocket motors.

The main attributes of EPDM rubber are its outstanding resistance to oxidation, ozonisation, and weathering effects. The most important properties from defence application point of view are its indefinite shelf life and excellent low temperature properties. Currently, a new class of EPDM, manufactured with constrained geometry metallocene catalyst, is available[18]. Technology also exists to the manufacture of EPDM for varying requirements in terms of physical forms, grades with heat and light stability, rheological properties with novel manufacturing methods. This helps to meet requirement of EPDM for a variety of industrial applications like wire and cable insulation, roof sheeting, extruded profiles, and white tyre sidewalls[19]. Granular EPDM manufactured in gas phase has been found to produce high performance products at lower costs[20]. The analytical techniques developed[21] provide a fingerprint of EPDM polymer. The developments in EPDM in the recent years are encouraging and indicate that this polymer is all set to gain an important status in the field of rocketry also.

2. REQUIREMENTS OF INSULATORS

Some of the specific requirements of an elastomeric insulator are:

- Excellent bonding of the insulator with propellant and motor case over the entire range of working temperature.
- Insulator propellant adhesion to be independent of curing characteristics of the insulator.
- Low ablation rate (0.09 mm/s to 0.2 mm/s) and low density (1.05 to 1.10) to minimise the inert mass of propulsion unit.
- Low thermal conductivity (4 to 5 x 10^{-4} Cal/cm/°C) and high specific heat (0.4 to 0.5 Cal/g/°C).
- Porous char with good retention characteristics.
- Ability to withstand mechanical and thermal stress during storage, handling, and curing operations.
- Low moisture absorption.
- Good ageing characteristics (minimum 10 years of shelf/useful life).

3. EMERGING TRENDS

Ethylene-propylene diene rubber called as EPDM (where M indicates that the polymer backbone chain consists of methylene units), manufactured by solution/suspension polymerisation[22], is basically a terpolymer, made of ethylene, propylene, and a diene (1,4 hexadiene, ethylidene norbornene or dicyclo pentadiene) in varying ratios. Depending on the application requirement, ratio of ethylene, propylene, and diene can be varied during manufacture.

3.1 Composition

Normally, composition of insulation consists of EPDM rubber as primary polymer and as secondary polymer to enhance the bonding properties[23-25] as EPDM alone gives inferior bonding characteristics. EPDM insulation compositions with carbon fiber[23], aramid fiber[23], silica powder[23] and asbestos[24] have been used successfully in rocket motors and gas generators. Incorporation of fibrous filler in EPDM facilitated by using liquid EPDM in the solid rocket motor insulation composition has also been reported[25]. Various additives such as fillers (particulate and fibrous), plasticisers, activators, accelerators, curatives, antioxidants, propellant-bonding agents, and a flame retardant are normally included in the insulation composition. A typical formulation[26] for EPDM insulation is given in Table 1.

3.2 Primary Polymer

EPDM with dienes such as 1,4 hexadiene (HD) or ethylene norbornene (ENB) has been reported as a suitable primary polymer in successfully developed insulation compositions[27]. Allen[28] has discussed the various advantages of high ethylene content EPDM rubbers like faster and smoother extrusion with high green strength that improved shape retention of the extrudate. In addition, crosslinking efficiency

Table 1. Typical formulation for EPDM insulation

Ingredients	Parts per hundred of rubber (phr)
Primary EPDM terpolymer	70 – 80
Secondary polymer	15 – 25
Tackifier	5 – 10
Anti-oxidant	1 – 3
Wetting agent	0 – 1
Cure activator	5 – 10
Silica filler	40 – 50
Pigment	0 – 3
Plasticiser	15 – 25
Curing agent	10 – 20

also improves since there are fewer chances for chain scission in ethylene sequences. The relationship between ethylene content and crystallinity has been discussed. Crystallinity and curing rates were found to increase with the increase in ethylene content[29]. Further, ethylene content is also found to have pronounced effect on mechanical properties[30]. The reported literature indicates that higher ethylene content is a better candidate for a primary polymer (among the various grades of EPDM) for rocket motor insulation compositions.

Among the commercially available grades, EPDM based on 1,4 hexadiene (NORDEL 1040, 2522, 2722) ENB (KELTAN 4506, 1446 A, 2308, NORDEL IP NDR 4520, and NORDEL IP NDR 4640) have reportedly been found suitable for rocket motor insulation[26, 31].

3.3 Secondary Polymers

With EPDM as a primary polymer base, polymers such as liquid polybutadiene[15], liquid EPDM[23, 26, 27] and adhesion-promoting polymers such as Hydroxy-terminated polybutadiene (HTPB)[32], neoprene[33] and hypalon[33] have been found successful as secondary polymers. Blends of EPDM–HYPALON were found effective in application like insulation, semiconductive shield and sheath compound[34].

Liquid EPDM (Trilene 65, 77), when employed with Kevlar™ fiber, has been found to provide good ablation and tear resistance[35], and when used in place of process oil, increases the modulus and hardness[36]. The successful performance of EPDM-based insulation in SRM with chlorosulphonated polyethylene and polychloroprene as secondary polymers has been reported[37]. Phenolic resins, when employed as secondary polymer, are reported to increase char formation and enhance erosion resistance[15]. Depending on the functional requirements of the insulator formulation, polychloroprene, chlorosulphonated polyethylene or liquid EPDM can be used as suitable supportive secondary polymer.

3.4 Fillers

High levels of reinforcing particulate fillers (up to 40 % by weight of the elastomeric insulating materials) can be used for suitably tailoring the modulus[14]. Selection of particular grade of EPDM and filler depends on the design specifications[38]. Both particulate and fibrous fillers have been used successfully with EPDM insulation[33]. High abrasive furnace grade (HAF, N 330) carbon black[15, 18] has been used both as a pigment and as reinforcing filler. The use of silica[4, 23, 25, 26], non-reinforcing filler, in EPDM insulator formulation was found to improve the mechanical properties. The use of precipitated silica in rubber compounding has been discussed in detail,[39] but precipitated silica being hydrophilic in nature, is found to absorb moisture leading to poor bonding characteristics of the insulation[41]. The replacement of hydrophilic silica with hydrophobic silica was found to improve the physical properties and reduce the moisture sensitivity of the insulation[31].

Carbon, aramid, and polybenzimidazole[4] fibres are found successful with fillers like carbon black and silica. Polyaramid pulp used as low-density filler not only enhances the mechanical properties of the insulator but also forms a strong and adherent char after propellant combustion. A low-smoke formulation has been identified with polyaramid pulp as a filler[41].

A comparative study between a non-fibre filled (K 380 B) and a fibre-filled (RM–468) formulation revealed that the latter had better ablation resistance, improved processability and superior tear strength, high tensile strength, good elongation and enhanced shrink resistance[25].

Kevlar™ fibres when incorporated in various rubbers like EPDM, silicone, polybutadiene, and polyisoprene, provided the required erosion resistance for long-burning duration motors and their performance have been found satisfactory[42].

Glass fibre has also been used as a compounding ingredient to improve the ablative efficiency[43]. Even though asbestos can be employed as potential fibrous filler, environmental and health concerns have led the manufacturers to seek an acceptable replacement for asbestos in rocket motor case insulation[40]. These inventions infer that promising formulations could be obtained with particulate filler like silica in combination with fibrous filler.

3.5 Curatives

EPDM insulator formulations can be cured with similar curatives that are employed for curing of EPDM rubber[4, 23, 25, 26]. For improved resistance to bloom and scorch, polymeric/insoluble sulphur can be a better choice[44]. When employing insoluble sulphur for curing, addition of napthenic oil is found to minimise dust explosion danger[45]. EPDM insulator formulations have been developed with a curative package of insoluble sulphur, mercaptobenzthiazole (MBT) and tetra methyl thiuram disulphide (TMTD)[46-49]. Solubility limits of various accelerators used in EPDM[50], given below, provide a guideline for deciding the combinations of the curative package.

MBT, Dibenzthiazyldisulphide (MBTS)	3.0 phr
Cyclohexyl benzthiazyl sulphenamide (CBS)	3.0 phr
Zincmercaptobenzthiazole (ZMBT)	3.0 phr
Dithiodimorpholine (DTDM)	2.0 phr
Zincdibutyldithiocarbamate (ZDBDC)	2.0 phr
TMTD, Zincdimethyldithiocarbamate (ZDMDC)	0.8 phr
Zincdimethyldithiocarbamate (ZDBDC)	0.8 phr
Tetra ethyl thiuram disulphide (TETD)	0.8 phr
Dipentamethylene thiuram tetra sulphide(DPTTS)	0.8 phr

When compared with sulphur curatives, peroxides provide better heat ageing properties and compression set[51]. The improvement in scorch resistance has been realised with the use of Luperco SRL organic peroxide in curing EPDM rubber formulations[52]. Peroxide curing imparts better ageing characteristics as compared to sulphur curing[53].

1,6 - bis (*N*, *N*' dibenzylthio carbamoyl dithio) hexane reported[54] as a crosslinker for diene rubber has proved to have excellent reversion and heat stability with no deterioration in the dynamic properties.

3.6 Additives

Additives such as processing aids, flame retardants, coagents (in case of peroxide curing), fatty acids for lubrication, talc or other whitening agent, antioxidants, etc play a major role in rubber formulation even though added in small amounts.

3.6.1 Processing Aids

Processing performance can be improved by the addition of processing aids as these lower the viscosity of the batch, thus reducing the mixing energy and time. Kastein[55] has discussed various processing aids suitable for the EPDM. Aromatic processing oil[46-49], hydrocarbon oil, etc have also been found suitable for EPDM insulation[42].

Godail[56] has discussed the effect of viscosity, aromatic content, volatility, colour stability, and specific gravity of aromatic, napthenic, and paraffinic petroleum extender oils on EPDM rubber compounding. Allen[28] suggests the use of napthenic oils as preferable plasticisers for EPDM compounds because these provide best compatibility. Stearic acid, zinc stearate and other internal lubricants are often used as processing aids. Usually 1-3 phr of processing agents are recommended for use. STRUKTOL HPS 11, a blend of fatty acid derivatives and STRUKTOL WB 16, a mixture of fatty acid soaps, are exemplary processing aids for EPDM insulation[40]. A reduction in melt viscosity is obtained when paraffinic oil is used[57].

3.6.2 *Flame Retardants*

It is reported[15, 25] that elastomeric insulating compositions include flame retardants selected from chlorinated compounds, antimony oxide and their combinations. Chlorinated organic compounds[15, 25] can be used with antimony oxide or hydrated alumina to enhance flame retardance. One of the chlorinated hydrocarbons used for this purpose is dechlorane, a flame retardant[15, 25, 26, 41].

3.6.3. *Additives For Ablation Rate and Erosion Rate Modification*

Resins such as phenolics[26, 41] and silicone[40] are found useful for increasing char formation, erosion resistance, and heat resistance. A combination of ammonium sulphate and antimony oxide gives a synergistic effect that reduces the ablation rate significantly[25].

It is reported that Ageriteä resin[26, 40], a phosphite antioxidant, provides a source of phosphorous in the maleated EPDM[40] insulation composition for low density and suitable charring, ablative performance.

Various char promotors like phosphorous compounds, boron compounds, ferrocene, halogens, and nitrogen compounds[58] can also be included in the formulation.

3.6.4. *Antioxidants*

Harpell[59] reports that quinoline-type antioxidants are preferred over other antioxidant types for peroxide cures of EPDM as these least interfere with the cure reaction. An antioxidant from bisphenol compounds has been found[60] to provide best protection.

Preferred antioxidants reported for EPDM insulation are 1,2-dihydro-2,2,4-trimethylquinoline and mixed ocylated diphenylamine[26, 37]. Styrenated phenol has also been used as an antioxidant[26].

3.6.5 *Tackifiers*

Tackifiers[26, 40] used in the formulation are hydrocarbon resins such as Wingtack 95, Akrochemä P-133, etc. A new polymeric tackifier based on Levopren VPKA 8696 designed for peroxide-EPDM applications, shows excellent peroxide compatibility with superior tack efficiency, when compared to the conventional naptha resins[61].

3.6.6. *Lubricants/other Additives*

Lubricants have been studied[63] as processing promoters and show higher scorch resistance, product performance, and processing speed. Baarle[63] suggests the use of semipermanent mold-release agents or permanent coatings for reducing mold fouling during the vulcanisation of EPDM rubber.

3.7 Processing Methodology

There is no common processing methodology for the available types of EPDM compounds due to wide variety of polymers and a wide range of compound specifications with different types of fillers, etc. However, broad guidelines have been suggested[54].

Low viscosity, high-propylene EPDM types mix well in the two-roll mixing mill. Warming of mill up to 60 °C may be used with slightly higher ethylene EPDM. High viscosity EPDM are difficult to mix in a two-roll mixing mill since these are usually highly loaded with fillers and oils. Banbury mixer is preferred for this type of EPDM[53]. The optimum mixing of high green strength EPDM rubber with additives in an internal mixer is achieved when the rubber used is in friablebale or crumb form[64].

The basic requirement of EPDM processing for rocket motor insulation is the compounding of the insulating material at a temperature below which the elastomer does not cure and permit the loss of compounding ingredients. Normally, the safer processing temperature was found to be around

90 °C. Conventional mixing and milling equipments can be used in compounding[26], followed by calendering to yield sheets[65].

Uniform dispersion of the fibre and the reinforcing filler is one of the major problems associated with mixing fibre-loaded compositions. A solvent-free method describes[23, 27] the incorporation of fragile carbon fibres in the EPDM polymeric matrix via distributive/reduced shear mixing without excessive fracture or fragmentation of the fibre. Controlled processing is recommended when incorporating polybenzimidazole fibres, as these have the tendency to break during processing[66].

Master batches of the rubber formulations were prepared in a standard manner using a Banbury mixer for compounding and mixing. For carbon and aramid composites, the required amount of fibre was added to a portion of a rubber masterbatch on a two-roll mixer mill. The samples were milled for a sufficient duration to disperse the fibres in the matrix at a mill opening of 1.5 mm. The milling direction was always kept the same to give the maximum amount of fibre alignment[67]. The developed and designed methodology for mixing/blending, optimised sequence of addition of ingredients pertaining to the development of EPDM insulation, has been discussed[33].

3.8 Ageing Characteristics

Deuri and Bhowmick[47] have studied the ageing characteristics of three grades of EPDM having different types of dienes. The findings show that post-curing reactions as well as destruction of crosslinks take place in the ageing process and the predominance of the former or latter depends on the structure of the diene. In general, retention properties of ENB-EPDM are found to be the best.

Successful launching of the rocket depends greatly on the mechanical as well as the ageing properties of the insulator. The thermal stability of EPDM can be attributed to its saturated main chain structure[68]. Curing and thermal ageing of EPDM synthetic elastomers have been studied using both ^{13}C high resolution and H^1 wideline solid state NMR techniques[69]. The kinetic parameters for degradation of EPDM with different types of fillers were studied using DTA and TGA at high temperature and the lifetime of the rocket insulator compound has been predicted[48].

Ageing study of EPDM rubber filled with cork, asbestos fibre, and iron oxide, carried out in the temperature range 100-180 °C in atmospheric air and nitrogen, showed that properties such as tensile strength, tear strength, and hardness increase with increasing time and temperature of ageing[49].

Stress relaxation of unaged and aged solid propellant insulator compounds based on EPDM has been investigated. It has been revealed that a thin coating of HTPB rubber on the insulator compound serves as a protective layer in the relaxation process for the insulator compound under stress[70].

3.9 Bonding of Insulation

As discussed, the success of insulation lies in satisfactory bonding with the propellant and with the metal case. Non-polar EPDM matrix shows inferior bondability with composite propellants based on HTPB. The advantage of better thermal properties and lower density of EPDM is made use in modifying the EPDM matrix with diol ingredients like HTPB, PTMO, and PEG for propellant bondability improvement. A comparative study shows that Kevlar-filled EPDM formulation and PEG-EPDM have improved bond strength[10].

The bondability of EPDM elastomer may also be improved by the oxidative degradation of EPDM rubber using phase-transferred permanganate as oxidant[71] and UV treatment[72].

Primers such as Chemlok 233 or a combination of Chemlok 200 B and Chemlok 234 B have been reported to enhance bonding of the elastomeric insulating material with the motor case[15].

The methods of bonding solid propellants to the insulation of rocket motor cases have been discussed[73]. Formulations with improved peel strength are also reported[25].

3.10 Shelf Life of EPDM Formulations

Curing agent activity has been studied for the storage life of EPDM formulations and it has been revealed that the number of curing agents employed should be compatible with the overall EPDM formulations to permit a satisfactory shelf life[26].

Ageing studies of two lots of uncured Neoprene FB (11yr and 8 month old) predicts 12.7 and 76 yr of shelf life if stored under cold storage temperature[75] of 4.4 °C. Eran[75], *et al*, have modelled the shelf life of EPDM components to be 363 year.

3.11 Ablative Properties

Polymers and rubbers, being low-conductive materials, are employed as ablative materials in applications requiring thermal protection of rocket hardware from high temperature combustion gases inside the motor[76]. The higher the thermal stability, the higher is the amount of char produced[77]. Under ablation and attack of hot gases and particles, the insulation gradually thins out and takes away significant quantity of heat, and hence, the chamber wall is effectively protected. Thus, these also act as ablative materials in addition to insulating the SRM. Various methods have been described for ablation test[78]. The fundamental aspects of erosion, decomposition, and char have been discussed[41].

The erosion capabilities or material-affected rate (MAR) of candidate rubbers have been summarised and Kevlar content in EPDM formulation has been found to improve the ablation capability under dynamic loading[79]. Hongging He[80] has reported EPDM as a good protective material with excellent charring characteristics. Tian[81] has experimentally obtained the charring ablation characteristics of solid rocket motors with EPDM as forward-dome insulator in the accelerated environment.

4. RECENT PROGRESS

Various grades of EPDM such as Nordel 4640, Nordel 4520, Herlene H-512, and Herlene H-563 were studied as primary polymer base[33]. Hypalon and neoprene were found suitable as secondary polymers to introduce polarity in the primary polymer. Liquid EPDM (Trilene 77) was used as secondary polymer with the incorporation of Kevlar and carbon fibres as fillers. All the formulations were studied and optimised with fibrous and particulate fillers like precipitated silica, fumed silica, Kevlar and carbon fibres. The compounds were cured with both sulphur and peroxide curing systems. Cure optimisation was carried out using Mooney viscometer and oscillating disk rheometer. Cured EPDM sheets were characterised for mechanical, thermal and interface properties. With the selected EPDM blends of various formulations, ballistic evaluation motors were insulated, composite propellant was cast in these motors, and successful performance achieved during the static testing carried out in radial and end-burning propellant modes. The data generated is yet to be published.

5. FUTURE SCOPE

Since enhancement of the shelf life of rocket motors is a mandatory requirement for the current and futuristic defence needs, there is further scope in this direction to develop an EPDM-based insulator with enhanced shelf life (preferably more than 10 years at ambient storage). The authors are engaged in this study.

ACKNOWLEDGEMENTS

The authors are grateful to Shri A. Subhananda Rao, Director, High Energy Materials Research Laboratory (HEMRL), Pune, for his encouragement during the course of this study and for according permission to publish this review. Authors are also thankful to Shri A.K. Mondal, Joint Director, for providing necessary support and facilities during literature survey and for constant encouragement.

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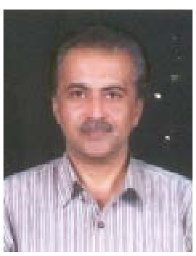
Contributors

Ms C.M. Bhuvaneswari obtained her BTech (Chem Eng.g) from the Regional Engineering College, Trichy, in May 2001. She joined DRDO at the High Energy Materials Research Laboratory (HEMRL), Pune, in 2001.Presently, she is working as Scientist C. Her area of research includes polymers in rocket propellants.

Mr M.S. Suresh Kumar obtained his MPhil from the Bharathidasan University, Trichy, in 2005. He joined DRDO at the HEMRL, Pune, in 2001.His area of research includes polymers in rocket propellants.

Dr (Mrs) S.D. Kakade obtained her PhD from the University of Pune in 1987. She joined DRDO at the HEMRL, Pune, in 1988. Presently, she is working as Scientist E. Her area of research includes polymers in rocket propellants. She has published 20 papers in national/international journals.



Dr Manoj Gupta obtained his PhD from the University of Pune in 2001. He joined DRDO at the HEMRL, Pune, in 1985. Presently, he is working as Scientist F. His area of research includes composite propellants. He has published 10 papers in national/international journals.