A.1.4 Développement de polyoléfines fonctionnalisées à partir d'élastomères thermoplastiques et de composites pour l'isolation des câbles Moyenne Tension. Préparation, caractérisation et prédiction de la durée de vie par des techniques de thermoanalyse.

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A.1.4 Development of functionalized poly-olefins based thermo-plastic elastom (TPEs) and composites as insulating mate for medium voltage cables. Preparation, characterization and life time prediction by thermo analytical techniques.

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A B S T R A C T

Attempt is made to develop a novel series of insulating material based on thermoplastic elastomers (TPEs) and blend composites for low to medium voltage applications. These have been prepared from the blends of PE-EPDM and PE-EPR using the ratio of 30:70. In the cases of TPEs rubber phase have been vulcanized dynamically at a temperature of 160°C. Either or both of the phases have been modified by peroxide initiated grafting of dibutyl maleate and vinyl silane in the Brabender plasticorder at the temperature ranging from 140°C to 200°C. Optimised peroxide (0.2 - 0.5%) and monomer (2 - 10%) concentrations have been used for grafting. Peroxide, peroxide sulfur and accelerated sulfur have been applied for dynamic curing. Filled and unfilled composites have been made by simultaneous blending of PE and EPR and grafting of vinyl silane on to it followed by co-crosslinking at ambient temperature. Silane modified compounds (TPEs and composites) are superior in terms of mechanical properties, oxidative degradation and ageing resistance properties. Life time of TPE at service tempe-rature (70°C) and at short circuit temperature (250°C) has been calculated as 10 -12 years and 35 - 40 minutes respectively. Thorough mechanisms of grafting, cross-linking and polymer-filler interactions have also been provided.

INTRODUCTION :

Thermoplastic elastomers (TPEs) based on polyethylene or polypropylene -polyolefin rubber blends have received considerable technological importance in recent years because of their ease of processing, possibility of reprocessing, low cost and favourable physical properties. Large number of efforts have been expended to make it viable for product applications (1,2,3,4). The authors have made an attempt to exploit these for application in low and medium voltage insulations as well in non / low halogen sheathing compounds by introducing structural changes in the blends (5,6).

Crosslinking of polyethylene (PE) and ethylene diene rubber (EPDM) and their blends improves the thermal endurance(7), continuous operating temperature and short ciruit temperature in the case of cable insulation. It has been reported by several authors that dynamically vulcanized rubbers resulted in an improved high temperature modulus over conven-tionally vulcanized blends (1 - 4). Effect of peroxide crosslinking on the high temperature modulus, crystallization and fusion behaviour of the PE-EPDM blends have been reported by the authors (7). Though dynamic vulcanization improves the high tempe-rature properties it is not possible to directly apply these TPEs for cable insulation mainly due to its inability to meet the hot elongation and hot set properties as per specification B.S.6899:1984. The technological properties of these TPEs can be further improved by promoting the inter-actions and interfacial adhesion between the plastic and elastomeric phases. The interactions between the components phases can be achieved through the modification of either or both the phases as well as by using the functionalized polymers as compatibilizer which interact with both the phases or by specific reactions between the two phases (5,6,8,9). However, reports on polyolefin based TPEs made for cable insulation are very few.

After installations the cables operate under a voltage stress of 30 to 70 V/mil (average stress) and the temperature may rise upto 50 to 60°C (10). However, the industry specification allow the conductor temperature to rise as high as 75 to 90°C for crosslinked PE, EPR, EPDM and their substitutes. Allowable thermal overload conditions are 130°C at the conductor. But the prolonged exposure to heat causes the ageing of the insulating material and its performance deteriorate due to chemical degradation. So, studies on the ageing of TPEs as insulating material are of relevance in view of the service life and performance of the cables. As the ageing of the material will depend on the nature of the filler, polymer-filler interactions etc., it is important to know the ageing of TPEs without filler and antioxidant. Although few investi-gations have been done on ageing of EPDM (11, 12), a few informations are available for polyolefin based TPEs and related materials(4). It is expected that ageing of thermoplastic vulcanizates changes the network structure of elastomer considerably, which in turn controls the technical properties. These changes are again dependent on time and temperature of ageing. So, ageing studies are also essential for an understanding of thermal and thermo-oxidative degradation of this compound.

In the present investigation attempt is made to develop a novel series of insulating material based on TPEs and blend composites using PE, EPR, EPDM and functionalized polyolefins. Techniques of functionalization, preparation of TPEs and comparative properties have been reported. Efforts have also been made to calculate the service life of the insulating materials through the high temperature ageing and degradation studies.

EXPERIMENTAL :

MATERIALS

Low density polyethylene (LDPE) (Neste Polyethylene DFDS-4445 of Neste Polyeten AB, Sweden) of density 0.915 g.cm^{-3} and MFI 2.0 g (10 min)$^{-1}$ (ASTM D-1238), ethylene propylene dicyclopen-tadiene terpolymer (EPDM) (KELTAN 520 of DSM, Netherland), Ethylene Propylene Rubber (EPR) (Vistalon 808 of Exxon Chemical Inc, Belgium), dibutyl maleate (DBM), Vinyl Silane (VS), dicumyl peroxide (DCP), Sulfur (S), tetramethyl thiuram disulfide (TMTD), merceptobenzthiazyl disulfide (MBTS) and other ingredients were used as received.

GRAFT MODIFICATION, MELT MIXING AND PREPARATION OF TPEs

Grafting of DBM and VS onto PE, EPR and EPDM as the case might be were carried out in a Brabender Plasticorder (PLE 330) using a cam type mixing head (N-50H). Different blend composition were made in the same mixer.

Infrared Spectroscopy : Infrared Spectroscopy was carried out by SHIMADZU IR-420 using thin film of polymer. Free DBM and VS were removed by acetone extraction of the film.

Mechanical Properties :

Tensile properties were studied by Zwick UTM (Model 1445) using dumbbell specimen (ASTM D 412-80)

Thermogravimetry : A METTLER TG 50 of a TA 3000 System with TC 10A microprocessor was used throughout the study. The heating rate was 20°C per minute.

Volume Resistivity : Volume Resistivity was measured by Hewlett Packard 4329A High resistance meter, according to the specification ASTM D 257-88.

Hot Elongation and Set Properties : Hot elongation and Set properties were carried at 250°C under a load of 20N as per the Specification BS:6899:1984.

Air Oven Ageing : Air ageing was carried out at different temperatures for different extent of time in Ceast Modular System Oven.

RESULTS AND DISCUSSION :

Functionalization of polyolefins and its characterization :

PE, EPR and EPDM were functionalized by grafting dibutyl maleate (DBM) and Vinyl Silane using DCP as initiator at the temperature ranging from 140°C to 200°C. The optimum concen-tration of monomer (2 -10%) was used for graft modification of the polymers depending on the type of monomer and according to the requirement. Due to corrosive nature and toxicity of the maleic anhydride it was not used for optimisation and further studies. Similarly 0.2 to 0.5% of DCP as initiator was used depending on the nature of monomer. IR Spectra of Polyethylene-g-DBM, Polyethylene-g-vinyl silane and Polyethy-lene are shown in Fig.1. DBM functionalized polymers show a strong absorption peak at 1738 cm^{-1} associated with stretching absorption of >C = 0 in the ester groups; of the maleate moiety. Absorption peak at 1090 cm^{-1} shows the presence of silane group on polymers. The detail methods of grafting has been described elsewhere (5,6). The mechanism of DBM and silane grafting onto PE is shown in Fig.2.