Chapter-2

Literature Review

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2.0. Introduction:

There is much interest in thermoplastic elastomers (TPEs) as it is the fastest growing field in the polymer industry. TPEs can be used in almost all industries and this creates a growing number of people that find it beneficial to understand their characteristics and to keep abreast of development of TPEs. With the growth, there is an increasing number of TPE product families that have been commercialized. Thus matters have become even more complicated as the number of commercial products in these families has rapidly multiplied.

Thermoplastic elastomers (TPE) sometimes referred to as thermoplastic rubbers are a class of polymeric material that behave mechanically like an elastomer at ambient temperature, yet can be processed like thermoplastic.

A TPE generally has a structure with microscopic-sized phases where one is of low modulus and easily deformable, and the other is rigid and acts like a link between the soft, flexible regions. This characteristic makes the TPE bulk mechanical behavior to change between a flexible softer polymer and a molten polymer fluid. When the TPE is heated above the melt transition temperature, the rigid phase will melt and allow the polymer to flow in processing equipment.

It is the crystalline domains that act as the “heat-fugitive cross-links” that give TPEs their thermoplastic character and the amorphous domains that give them their elastomeric character. The crystalline domains are typically referred to as the “hard” phase and the amorphous domains as the “soft” phase. While both phases contribute to the overall physical and mechanical properties of a TPE, some key properties may be associated with one phase or the other which help in guiding the selection of the phases or in designing a TPE compound.

The principal difference between thermoset elastomers and thermoplastic elastomers is the type of crosslinking bond in their structures. In fact, crosslinking is a critical structural factor which contributes to impart high elastic properties. The crosslink in thermoset polymers is a covalent bond created during the vulcanization process. On the other hand the crosslink in thermoplastic elastomer polymers is a weaker dipole, or a hydrogen bond or an ion induced dipole interaction.
The different TPE families come from the different chemistry of the polymers employed. A number of TPE families have a polymer that consists of rigid and flexible regions within the polymer molecules itself. These are the block copolymers which include the styrenic block copolymers (SBCs), thermoplastic urethanes (TPUs), copolyester block copolymers (COPEs) and polyamide block copolymers (COPAs).

Other families consist of blends of rigid and flexible polymers that are compatible enough to have two phases that bond well. These blends include the thermoplastic olefin blends (TPOs) and PVC/nitrile rubber blends (PVC/NBR). Another type has separate rigid and flexible polymers that have been chemically reacted to have enhanced mechanical properties, particularly where the elastomer phase has been cross-linked. The TPEs with a cross-linked elastomer phase are thermoplastic vulcanizates (TPVs) and generally achieve mechanical performance in the same class as thermoset (cross-linked) rubbers. The proliferation of products in each of these areas has continued and particularly in the TPVs there has been a lot of development.

Developments in TPVs have continued to grow pretty rapidly since it has the highest growth rate of the TPE families. The highest volume TPV is based on an EPDM cross-linked rubber phase and polypropylene plastic phase (EPDM/PP TPV). Recent developments in this family of products have included improved cross-linking chemistry to provide an improved TPV property.

Several new types of TPVs have been introduced more recently including one with a silicone rubber phase and an engineering thermoplastic phase. It is referred to as TPSiV. TPSiVs have a silky feel in the softer grades and can be used continuously to 140 – 150°C.
2.1. Literature review on TPV from olefinic thermoplastic and various elastomer:

Indose Aravin and Sabu Thomas [1] reported the rheology and morphology of uncompatibilized and reactively compatibilized blends of polytrimethylene terephthalate and ethylene propylene diene monomer & tried to establish a correlation between them.

Polytrimethylene terephthalate (PTT)/ethylene propylene diene monomer (EPDM) blends are a new class of thermoplastic elastomers that combine the excellent engineering properties of PTT with the elastic, ozone, and weathering resistant characteristics of EPDM.

The authors analyzed the effects of compatibilization on the rheology and morphology of PTT/EPDM blends using ethylene propylene copolymer-grafted maleic anhydride (EPM-g-MA) as compatibilizer. They used the Palierne and Choi-Schowalter models to calculate the interfacial tension and correlate the rheology and phase morphology [2, 3].

The complex viscosity (\(\eta^*\)) of uncompatibilized PTT/EPDM blends decreases with increasing frequency. The viscosity ratio is very sensitive to frequency fluctuation because of the highly incompatible nature of PTT and EPDM. The phase morphology of uncompatibilized blends revealed that all blend composition, except PTT_{60} and PTT_{50} (subscript denotes the % of PTT), have a typical matrix/dispersed phase morphology. The average domain size (Dn. Dw: Number and weight-averaged sizes) of dispersed particles indicates that all blends exhibit a non-uniform and unstable morphology.

As the wt % of the minor component in the blends increases, the non-uniformity increases, with a simultaneous decrease in stability. Thus, they observe good agreement between rheology and morphology.

Their studies further showed the effect of compatibilization on the complex viscosity of PTT_{70} blends: \(\eta^*\) which usually increases up to a critical compatibilizer concentration (CMC). This is taken as evidence for the compatibilizing action of EPM-g-MA through interfacial chemical reaction, which enhances the favorable interaction between the polymer chains at the interface,
consequently increasing the system’s viscosity. Above the CMC, \( \eta^* \) levels off. This is an indication of interfacial saturation, followed by micelle formation.

The Dn and Dw values of compatibilized PTT\(_{70}\) blends exhibit a reduction in particle size with increasing compatibilizer concentration. This is caused by the reduction in interfacial tension and coalescence rate as a result of emulsification. After the initial sharp decline in particle size, a quasi equilibrium state is reached above the CMC. Their experimental results indicate that the domain distribution becomes narrow in the presence of compatibilizer, indicating a finer, more uniform, and more stable morphology. Therefore, it is clear that the rheology and morphology compatibilized blends also correlate well.

Martin Van Duin [4] reported an overview of TPVs. Like other thermoplastic elastomers, TPVs combine the elastic and mechanical properties of thermoset crosslinked rubbers with the melt processability of thermoplastics. Emphasis is given on general purpose TPVs based on resol crosslinked EPDM/PP/Oil blends. The following aspects of scientific developments are discussed in detail: resol crosslinking chemistry, extruder dynamic vulcanization, TPV morphology, oil distribution, TPV elasticity model and TPV rheology. At last series of scientific question and technological problems which are challenging future TPV developments are put forward at the end.

In another report, Kentaro et al [5] described structure and mechanical properties of olefinic TPV. TPV is a special class of TPE, produced by melt mixing and crosslinking of EPDM with PP simultaneously. Recently, TPV has been widely used in many industrial applications, especially for environmental reasons such as recyclabilities, processing ease compared with vulcanized rubber and PVC replacement. The significance of the understanding of structure – properties relationship of TPV is increasing. The authors have investigated the correlation between the degree of crosslinking and particle size/distribution of EPDM phase and the resulting TPV compounds performances. Compression set properties, representing rubber elasticity of the TPV compounds and mechanical properties were improved with increasing crosslinking density of EPDM phase. By TEM analysis, TPVs with smaller particle size and particle size distribution showed better physical properties and rubber elasticity.
In another study, Fritz et al [6] reported on innovative TPV two-phase polymers stressing on formulation, morphology formation, property profiles and processing characteristics. The new TPV is composed of a PP–matrix in which a metallocene – type ethylene/octene copolymer (Eo) is dispersed. The Eo copolymers are grafted with vinyl organosilanes, then blended with PP, hydrolyzed and crosslinked in a co-rotating, intermeshing twin screw extruder. The resulting TPV grades are easy to process into article showing an attractive range of properties. The advantages of these TPVs are ascribed to blend composition and crosslinking concept. The new TPVs can be processed without pre drying. Mouldings are characterized by excellent surface quality and absence of odor as a result of the innovative use of Eo elastomer and the modified crosslinking concept. They can easily be coloured to any desirable shade. The reduced cost of ingredients is another advantage of the newly developed thermoplastic elastomers. High ultimate strength and elongation at break values as well as a broad spectrum of different Shore A grades open up many new field of application. The main focus has been on the auto motive applications because of very low fogging rates.

Cook et al [7] reported their invention on thermoplastic elastomer compositions. A thermoplastic elastomer comprises a blend of thermoplastic components (PE/PP) & a cured elastomer. The elastomer part consists of a major elastomer (cis-1,4 polyisoprene) and a minor elastomer. This minor elastomer is a high molecular weight reactive polymer (atactic high vinyl butadiene, syndotactic 1,2 polybutadiene, NBR with acrylonitrile content 18-20%) which shows higher cross linking efficiency than the major elastomer in free radical induced curing reaction. The minor elastomer preferably consists of 4-10 pbw per 100 parts of total elastomer present in the composition. The use of high molecular weight & reactive polymer as a minor elastomer component brings improvement in recovery properties, low temperature performance, processing characteristics, resistance to stiffening at low temperature. The major elastomer is preferably miscible with the minor elastomer component. TPE composition may be made by mixing the thermoplastic component with the major & minor elastomers (as described above) at a temperature such that the thermoplastic component melts to give a melt blend.
of the components. Then the elastomer components in the melt blend are subjected to cure in presence of an organic peroxide curative.

Yun et al [8] reported on development of high-performance styrenic thermoplastic vulcanizates (STVs) for long term high temperature applications. These STPVs consist of polypropylene as the continuous phase and a crosslinked modified hydrogenated styrenic block copolymer (mHSBC) as the dispersed phase. The present study compared STPVs with conventional TPVs (CTPVs) containing EPDM/PP. The STPVs showed a 20 % improvement in solvent resistance after 500 h of immersion in IRM 903 oil at 125°C, and the swelling of STPVs did not increase with time. The elastic recovery was 50 % better than what was achieved with CTPVs. Tensile property retention was approximately 10 % higher after aging for 1440 h at 125°C when compared to CTPVs. These specific improvement in properties for STPVs relative to the conventional TPVs can possibly be explained by the unique morphology of the STPV compounds. These performance characteristics make STPVs more suitable for high temperature air and chemical environmental applications. This new TPV technology is expected to bridge the gap between polypropylene/EPDM TPVs and more costly engineering TPVs.

In another study Leaversuch et al [9] informed about some commercially available super-TPVs. Recent commercialization of a cluster of novel thermoplastic vulcanizate (TPV) families is promising to boost demand for thermoplastic elastomers in new and challenging industrial and consumer product segments. One evolving class is “supper-TPVs” designed to replace high-cost thermoset rubbers and upgrade the performance of conventional TPVs in more extreme applications, notably auto under-hood, appliance, and industrial parts subjected to high heat (135 to 170°C) in the presence of oils and greases. The initial member of this new class consists of a cross-linked silicone rubber embedded in a nylon or TPU matrix. More recently, variations of this “thermoplastic silicone vulcanizate (TPSiV) family based on other engineering thermoplastic matrices are being developed.

A second new class of TPVs is also emerging to fill a mid-range performance level. These retain PP as the matrix, but incorporate a styrenic
elastomer as the vulcanized rubber segment. These TPVs improve compression set, oil resistance, and adhesion of conventional TPVs and are aimed at over molded high-performance grips, seals, and diaphragms.

DuPont has recently unveiled its “engineering TPV” (ETPV) family combining a copolyester matrix material with a highly crosslinked rubber as the vulcanized segment. The rubber is AEM, a modified ethylene-acrylate. DuPont ETPV is commercially used in spark-plug boots, truck air-brake hose, and fuel-vent hose. Other promising applications are ducting, ignition seals, body plugs, and CVJ boots.

Zeon Chemicals introduced a super-TPV combining nylon 6 as matrix with a cross-linked polyacrylate (ACM) rubber. The new grades withstand hot-oil immersion at 150°C over 3000 h.

The new TPSiV from Dow Corning possess abrasion resistance, good flame retardancy, excellent heat resistance in presence of hot fluid, plus significant improvements in processing that reduces scrap and overall cost. Other TPSiV grades have been engineered for communication devices, consumer goods, and medical devices. One example is the recent commercialization of mobile phone covers made of TPSiV, which reportedly outperformed other materials with a combination of high-temperature resistance, low-temperature flexibility, superior abrasion resistance, good bonding to thermoplastic substrates in two-shot molding, weathering resistance, colorability and processablity (reduced cycle times).

Verbois et al [10] reported a new thermoplastic vulcanizate composed of PP & EVA crosslinked by tetrapropoxysilane. A thermoplastic vulcanizate (TPV) is tailored by a dynamic vulcanization process. TPVs can be processed as thermoplastics and have properties similar to conventional vulcanized rubber. The main objective of their work was to tailor, by using the reactive extrusion process, a new TPV composed of polypropylene homopolymer (PP) as thermoplastic phase and ethylene-vinyl acetate copolymer (EVA) as elastomer phase, which is crosslinked by tetrapropoxysilane (TPOS) as crosslinking agent in the presence of dibutyl tin oxide (DBTO) as catalyst. Crosslinking is carried out through a trans esterification reaction between the ester groups of EVA and the alkoxysilane groups of TPOS. This exchange reaction is catalyzed by DBTO at temperatures
above 100°C. The main advantage of this chemistry is non-radical, and so prevents the degradation of PP, in comparison with crosslinking reactions using peroxides as initiators.

Different reactive blends were prepared in the internal mixer of a Haake Plasticorder. In order to know how the crosslinking reaction has advanced, the EVA gel content and the volume swelling rate of the blend were measured. The aim of this study was to get a better understanding of the dispersion mechanism of EVA in the major phase during its dynamic vulcanization in the presence of PP as the minor phase. This paper deals with the correlation that exists between the evolution of the two-phase blend morphology and the extent of the crosslinking reaction on the elastomer phase during the synthesis of a TPV. In particular, they showed that the correlation was almost the same of the elaboration of the TPV in the internal mixer of the Haake Plasticorder (discontinuous process) and in a twin-screw extruder (continuous process).

In another report Worley et al [11] described some high performance TPVs for long term high temperature applications. They developed a new type of TPV based on a modified hydrogenated styrene block copolymer with excellent elastic recovery (lower compression set) and high solvent resistant properties. A comparative study was reported on conventional TPVs (PP/EPDM) and the newly developed TPV. The styrenic TPV developed herein was based on modified hydrogenated styrene block copolymer (HSBC). Detailed structural information was not disclosed. This HSBC is believed to have reactive groups in the main chain. The typical TPV formulation consisted of HSBC, polypropylene, processing oil, curatives and additives. As the level of polypropylene increased and the level of oil decreased, the tensile strength increased. On the other hand, there is no effect of oil levels on compression set, but the compression set increased proportionally as polypropylene levels increased. The STPV shows a 10 % to 20 % higher tensile strength relative to the conventional TPV. The tear strength of STPV is at the same level as the peroxide cured conventional TPV (CTV1). The compression set and weight gain are reported as a function of hardness. The compression set of the STPV, relative to the various CTPV is lower by approximately 20 % even at 125°C. In oil resistance test the STPV has a much
lower weight gain than conventional TPV. It was noticed that STPV had excellent long term elastic recovery properties, based on compression set, that increased by only 5%. It is concluded that STPVs have a superior long-term elastic recovery and solvent resistance relative to conventional TPVs based on EPDM/PP blends. The properties of TPVs were compared in the same hardness range. It is observed that the properties of the STPVs were better balanced than those of the CTPVs, even though the STPV had slightly lower elongation at break. In particular, tensile strength, compression set and solvent resistance of the STPV were better than those of the CTPVs. After dynamic vulcanization, the morphology on a micro scale for a STPV is similar to that of a CTPV. However, the STPV has the subtle difference of nano phases (PS multi-junction) dispersed within the micro domains. This dual rubber phase network morphology with micro and nano scale rubber phases is likely to increase the crosslink density and elasticity of the rubber phase. This dual network morphology could explain the excellent long term compression set consistency (elastic recovery) and solvent resistance. One can conclude that the nano domain is a fairly unique feature of the STPV morphology when compared with a conventional TPV.

The developed (STPV) in comparison to the conventional TPV had a well-balanced mechanical profile that can be readily molded and recycled. These excellent long-term properties are explained by the dual rubber phase network generated by a modified HSBC.

Chung et al [12] reported a unique process for preparing TPEs by dynamic vulcanization through a patent. The process comprises melt mixing of a thermoplastic (PP homo polymer, Tm: 80-135°C & M.F.I < 1.2 g/10 min), one vulcanizable rubber (EPDM) and an additional engineering thermoplastic in the form of solid particles (with an effective diameter not less than 0.05 mm) & then subjecting the rubber for cross linking by a curing agent under high shear condition. Here an additional engineering thermoplastic is added to melt mixture of the first thermoplastic& rubber in the form of solid particles before, during or after addition of cross linking agent – but prior to substantial crosslinking of rubber. This process helps in providing a route to avoid substantial degradation or unwanted cross linking of the major or minor thermoplastic.
In another study Sarkhel et al [13] reported on dynamic vulcanization of polyethylene-based thermoplastic elastomer blends. This study evaluated the effect of the dynamic vulcanization of PE (LDPE or HDPE) – EPDM blends by sulfur on the mechanical, dynamic mechanical, electrical, thermal and morphological properties. The dynamic vulcanization of the EPDM phase dispersed in the PE matrix significantly improved the tensile and impact properties of the blends, and this indicated the formation of a crosslinked network structure in the rubber phase. The crosslinking efficiency of the PE-based EPDM blends upon sulfur curing was well evaluated with torque and gel content measurements. However, the HDPE-EPDM blend exhibited a more pronounced curing effect on the properties in comparison with the LDPE-EPDM blends. The sulfur-cured PE-EPDM blends exhibited better dispersion of the EPDM phases in the PE matrix in comparison with the uncured blends. The thermal stability and volume resistivity of the PE-EPDM blends were also significantly improved upon sulfur vulcanization, although the extent of improvement in the properties depended on the variation of the polymeric composition and sulfur dose in the blends. In SEM analysis, good interface bonding between the polyethylene matrix and dispersed ethylene-propylene-diene terpolymer was observed for the cured blends.

Nakason et al [14] reported on thermoplastic vulcanizates based on maleated natural rubber/polypropylene blends. The effect of blend ratios on rheological, mechanical, and morphological properties was discussed. Maleated natural rubber (MNR) was prepared and used to formulate thermoplastic vulcanizates (TPVs) based on various MNR/PP blends. The influence of mixing methods on the TPVs’ properties was first studied. The authors found that mixing all ingredients in an internal mixer provided the TPVs with better mechanical properties. The final mixing torque, shear stress, and shear viscosity of the TPVs prepared with various blend ratios of MNR/PP increased with increasing levels of MNR in the blends. This may be attributed to higher shear viscosity of the pure MNR than that of the pure PP. Furthermore, as evidenced in SEM micrographs, the TPVs exhibited two phase morphologies with dispersed small vulcanized rubber domains in the PP matrix. The higher content of PP caused the more molten continuous phase during mixing and rheological characterization. Tensile
strength and hardness of the TPVs increased with increasing levels of PP, while the elongation at break decreased. Furthermore, the elastomeric properties, in terms of tension set, increased with increasing levels of MNR in the blends. This may be attributed to decreasing trends in the size of vulcanized rubber particles dispersed in the PP matrix with an increasing concentration of MNR.

Lawrence et al [15] reported on crosslinking thermoplastic elastomer for improved product performance. A crosslinking TPE formulation was developed by taking a high-performance copolyamide resin and modifying it to perform in even more demanding applications. The material was shown to offer elevated heat resistance, improved chemical resistance, and increased tensile strength and toughness, among other improvements. High-temperature performance was especially notable. In fact, once crosslinked, the material can be used in temperature at and even above the melting point of the non-crosslinked resin. Available in a range of durometer rating from soft to semi rigid, the material can be used to produce thin-wall parts, tubing, wire-and-cable coatings, and other products that can benefit from these improved physical properties. This study demonstrates that it is possible to modify formulations and radiation dosages so as to tailor cross-linked materials to the properties most desired in specific finished products. Refinement – including ongoing work with alloys – continues to optimize the level of crosslinking and provide an improved balance of physical properties. The further development of crosslinked TPE compounds is certain to lead to the creation of new molded products possessing unique physical properties.

Nakason et al [16] reported on the effect of vulcanization system on the properties of thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends. Epoxidezed natural rubber with mole percentage epoxide of 30 was synthesized and used to prepare thermoplastic vulcanizates based on 75/25 ENR/PP blends with Ph-PP (phenolic modified PP) as compatibilizer. Influences of various curing systems (i.e., sulfur, peroxide and a mixture of sulfur and peroxide-cured systems) were investigated. The author’s found that the mixing torque, shear stress, shear viscosity, tensile strength and elongation at break of the TPVs using the mixed-cure system exhibited higher values than those of the sulfur and peroxide-cured systems, respectively. This may
be attributed to a formation of S-S, C-S combination with C-C linkages in the ENR phase. In the sulfur-cured system only S-S linkages are formed, whilst in the peroxide curing system more stable C-C linkages are formed. However, during shearing at high temperature of the peroxide and mixed-cure systems, the peroxide caused degradation of the polypropylene molecules. Higher level of DCP was used in the peroxide-cured system and caused greater influence on properties. In the mixed-cure system, lower influence of PP degradation and influence of formation of more stable C-C linkages overcomes the drawback of chain scission as mentioned above. Therefore, they observed the highest values of those properties using the mixed-cure system. The curing systems did not however affect the hardness properties and solvent resistance of the TPVs. They also found that the dispersed vulcanized rubber domains of TPV with the peroxide-cured system were smaller rubber particles than those obtained in the cases of the mixed and sulfur-cure systems.

Medsker et al [17] reported on hydrosilylation cross linking through a patent. Their invention is based on the discovery that the process for hydrosilylation cross linking of the rubber in a TPE can be more effectively carried out by using a platinum containing catalyst and a diene containing elastomer with sterically unhindered carbon – carbon double bond. This process requires very low concentration of catalyst, but provides rapid cross linking of the elastomer. Here no compatibilizer is required to achieve composition with excellent mechanical properties. In spite of using very low concentration of catalyst, the TPE obtained, was found to have much improved heat ageing characteristics, resistance to degradation by UV and non-hygroscopic character.

In another embodiment, authors reported the effect of using an oil, free of Lewis base, in dynamic vulcanization of a blend of thermoplastic and an unsaturated rubber in presence of hydrosilylation agent, Pt containing hydrosilylation catalyst & a process oil. Here authors found requirement of even lower concentration of catalyst for curing the rubber & resulting TPE was found excellent tensile properties, good heat ageing & UV resistance, no undesirable color & non hygroscopic character.
In a further embodiment of the invention, authors found that use of additives, which react with residual silicone hydride functionality in TPE, can produce TPE with improved heat ageing resistance characteristics.

The TPEs produced by the improved process can be used as replacement for thermoset rubber in different industrial application e.g., automobile underhood parts, mechanical rubber goods, hose, tubing, gaskets. These TPEs can be used for electrical application & household goods.

Sabet et al [18] reported on use of silane grafted polyolefin in EPDM/polyolefin TPV to enhance physical properties e.g., decreased compression set. They prepared a TPV from a semi crystalline polyolefin, an unsaturated rubber and a silane grafted thermoplastic polyolefin. Crosslinking of the rubber was effected by using hydrosilylation crosslinking agent. The silane grafted polyolefin facilitates interaction between the first TPO & the unsaturated rubber with its pendent OR group. Here R is H or an alkyl group. The pendent OR groups or its hydrolysis product can chemically bond with hydrosilylation cross linking agent. Thus the OR group can function as reaction site to bond the silane grafted polyolefin with the rubber via hydrosilylation crosslinking agent. The silane grafted polyolefin was used at a dose of 2-25 wt. % of the wt of said polyolefin and unsaturated rubber.

Moldvan et al [19] reported on EPDM-HDPE blends with different cure systems in respect of their mechanical and infra-red spectrometric properties. The physico-mechanical properties and the Infra-red (IR) spectra (obtained by applying the Attenuated Total Reflectance (ATR) technique) of high density polyethylene (HDPE)/ethylene propylene diene ter polymer (EPDM) blends were investigated using a Zwick Tensile Testing machine and a Fourier Transform Infra-red (FTIR) spectrometer. Three kinds of cure systems were used: i) sulfur, tetramethylthiuram disulfide (TMTD) and 2-mercaptopbenothiazole (MBT); ii) sulfur, tetramethylthiuram disulfide (TMTD) and zinc-diethyldithiocarbamate (ZDEC), iii) sulphur, TMTD & DPG. The composition of HDPE and EPDM was fixed at 50/50 by weight and the ratio of curing accelerators/sulfur was varied from 0.4 to 6.34 by weight. Results indicated that polymer alloys EPDM/HDPE containing cure agents, sulfur, TMTD and MBT, in a ratio of curing
accelerators/sulfur = 6.34 and 1.85, respectively, showed improved physico-mechanical properties as compared to the other polymer blends. This behavior was confirmed by the recorded ATR-FTIR spectra of the studied samples.

Nakason et al [20] reported on thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends the authors studied the effect of blend ratios of ENR/PP, types of compatibilizers & reactive blending. Epoxidized natural rubber (ENR) was prepared using the performic epoxidation method. TPVs based on ENR/PP blends were later prepared by melt mixing processes via dynamic vulcanization. Phenolic modified polypropylene (Ph –PP) and graft copolymer of maleic anhydride on polypropylene molecules (PP-g-MA) were prepared and used as blend compatibilizers and reactive blending components of ENR/Ph-PP and ENR/PP-g-MA blends. It was found that the mixing torque, apparent shear stress and apparent shear viscosity increased with increasing levels of ENR. This is attributed to the higher viscosity of the pure ENR than that of the pure PP. Furthermore, there was a higher compatibilizing effect because of the chemical interaction between the polar groups in ENR and PP-g-MA or Ph-PP. Mixing torque, shear flow properties (i.e., shear stress and shear viscosity) and mechanical properties (i.e., tensile strength, elongation at break, and hardness) of the TPVs prepared by reactive blending of ENR/Ph-PP and ENR/PP-g-MA were lower than that of the samples without a compatibilizer. However, the TPVs prepared using Ph-PP and PP-g-MA as compatibilizers exhibited higher values. We observed that the TPVs prepared from ENR/PP with Ph-PP as a compatibilizer gave the highest rheological and mechanical properties, while the reactive blending of ENR/PP exhibited the lowest values. Trend of the properties corresponds to the morphology of the TPVs. That is, the TPV with Ph-PP as a blend compatibilizer showed the smallest rubber particles dispersed in the PP matrix, while the reactive blending of ENR/PP-g-MA showed the largest particles.

Mishra et al [21] studied on preparation and properties of a new thermoplastic vulcanizate (TPV)/organoclay nanocomposite. A new thermoplastic vulcanisate organoclay nanocomposite was prepared using EPDM, PP and MA functionalized PP as elastomeric phase, thermoplastic and compatibilizer respectively. The x-ray diffraction (XRD) and transmission electron microscope
indicated the intercalation of polymer chains inside the clay layer. The tensile modulus of the only 5 wt. % clay-based nanocomposites is much higher than that of the 20 wt. % talc-based microcomposite. Dynamic mechanical analysis showed that the glass transition temperature of the ethylene-propylene-diene ter polymer phases of the nanocomposite remains the same, whereas that of PP phase is increased compared to the pristine counterpart of the nanocomposite.

Chatterjee et al [22] made a survey on development of thermoplastic elastomers based on maleated ethylene propylene rubber (m-EPR) and polypropylene (PP) by dynamic vulcanization.

Dicumyl peroxide (DCP)-cured thermoplastic vulcanizates (TPVs) based on blends of maleated ethylene propylene rubber (m-EPR) and polypropylene (PP) using maleated-PP as a compatibilizer have been developed. Physical properties of these TPVs change significantly with concentrations of DCP and rubber/plastic blend ratios. Important correlations were obtained from rheometer delta torque values with various physical properties of the TPVs like tension set and crosslink density etc. Wide angle x-ray diffraction study confirms that concentration of DCP has a strong influence on the crystallinity of PP, which might affect the final physical properties of TPVs. The recyclability and ageing characteristics of these TPVs are also found excellent.

Investigations were made by Nancy Boschert [23] on TPVs in medical application. Outcome of this study presented that medical grade TPVs possesses the required characteristic for replacing thermoset elastomers such as NR and silicone rubbers in many medical products. The mechanical performance and sterilizability of such TPVs are found quite acceptable for most applications. The materials seemed to offer real benefit to medical device designers is in the areas of biocompatibility and cost reduction. They will not however meet the needs of all applications. These TPVs lack the extraordinary resilience of NR, e.g., they do not perform as well in applications for which repeated needle penetration is crucial. However, they do seem to resolve some of the major materials problems experienced by the medical industry and warrant serious evaluation for use in a wide range of products.
Yoshihiro Soeda [24] reported on thermoplastic elastomer composition through a patent. They invented a TPE from thermoplastic PA resin (Nylon11, Nylon 6, 66), a halogen containing rubber (brominated isobutylenes-p-methyl styrene copolymer), and a molecular chain extender (hexamethylenediamine or 6 amino hexanoic acid). At first the thermoplastic & the unvulcanized rubber were melt kneaded in a twin screw extruder & the elastomeric part was cross linked by dynamic vulcanization using a suitable cross linking agent, while melt kneading in the same machine. During melt kneading, the temperature was at least the melting temperature of thermoplastic & the shear rate 1000 – 7500 s⁻¹. In this invention the composition ratio of thermoplastic PA/halogen containing rubber was 10/19 to 90/10 and the amount of molecular chain extender was 1-5 pbw per 100 parts (by wt.) of thermoplastic PA. In a TPE composition, where the elastomer component is dynamically vulcanized, the elastomer part is dispersed as fine particles in the thermoplastic matrix. In the present invention the object of using a molecular chain extender in a TPE composition was to increase the molecular wt. of the matrix – leading to increase in melt viscosity – thereby increasing the melting temperature. It will suppress the agglomeration of dispersed cross linked elastomer particles in the shaping process. So when this TPE will be used in forming a film – a uniform dispersion of cross linked rubber particles will be achieved.

Nader et al [25] made some studies on dynamic vulcanization of PP/NBR thermoplastic elastomer blends. In this work, selected grade of polypropylene (PP) was modified with dimethylol-phenolic resin and then it was melt-mixed with acrylonitrile-butadiene rubber (NBR) for several weight ratios. After sufficient mixing time additional phenolic resin was added to mixing chamber and the blends were dynamically vulcanized. In order to study the effects of the compositions and dynamic vulcanization on the physical and mechanical properties, simple blends of unmodified polypropylene and NBR were also prepared. The results show that dynamically vulcanized blends have higher tensile strength, elongation at break, solvent and oil resistance.

G. Ivan [26] reiterated on dynamic vulcanization as an accessible way to thermoplastic elastomers. In his review work, technical and economical reasons relating to the increased performance level, greater productivity, and the economic
use of materials and energy are stimulating the industry toward an accelerated increase in the use of thermoplastic elastomers. The thermoplastic elastomers obtained by mixing classical elastomers and plastomers form a class of materials with the largest prospect for commercial application. These materials are obtained by mixing rubbers with thermoplastics and realizing the crosslinking of the elastomer phase during a mixing operation frequently referred to as “dynamic vulcanization”. The nature and ratio of both polymers participating in the system are crucial for the main physical characteristics (young modulus, modulus at 100% elongation, etc.) and their influence on final properties (tensile strength, elongation at break, tears strength, etc.) and resilience. Here the parameters of mixing and the vulcanization operation as well as the properties of the resulting thermoplastic elastomers non-polar polymers are reviewed.

Soares et al [27] reported on a novel thermoplastic elastomer based on dynamically vulcanized polypropylene/acrylic rubber blends. Thermoplastic elastomer based on polypropylene and acrylic rubbers were studied with special emphasis on the effect of the reactive compatibilization and dynamic vulcanization. The compatibilization with maleic anhydride-function-alized PP/TETA system resulted in a significant improvement of mechanical properties and oil resistance. In addition, a significant improvement on the elasticity of the material as indicated by the lower tension set values and a lower stress relaxation were observed. The reactive compatibilization was also suggested by the increase of the torque during mixing and by the increase of the viscosity and storage modulus of the blends. The dynamic vulcanization process was only effective for compatibilized blends. For this blend, the vulcanized rubber particles presented lower particle size, which was effectively surrounded by the PP matrix, characterizing an actual thermoplastic vulcanize. However, superior mechanical performance and finer morphology with smaller rubber particle size were achieved for non vulcanized/compatibilized blends. Probably the decrease of the interfacial tension, the improvement of the interfacial adhesion and the crosslinking of the rubber particles, imparted by TETA in combination with PP-g-MA such improvements were effected. The reactive compatibilization also resulted in a decrease of damping and an increase of storage modulus obtained from dynamic
mechanical analysis and an increase of melting and crystallization temperature as a result of the mobilization restriction imparted by the chemical bonds at the interface. The PP/ACM thermoplastic elastomers presented good reprocessability.

Vennemann et al [28] determined of crosslink density of peroxide cured TPV. EPDM/PP model compounds were dynamically vulcanized by use of varying amounts of organic peroxide and a trifunctional methacrylate to produce thermoplastic vulcanizates (TPV) materials with different properties. Tensile strength and ultimate elongation as well as compression set data of these materials are comparable to the existing commercial TPV products. Although, crosslinking of the elastomer phase is the most important step during the production process, there is a lack of suitable test methods until now to determine the crosslink density precisely. Therefore, a new test method, temperature scanning stress relaxation (TSSR) was examined to determine the crosslink density of the EPDM phase. The results are in good agreement with results obtained from conventional swell measurements. The advantages of TSSR measurements over swell measurements are quite obvious. Whereas swelling measurements are very time consuming, TSSR tests are much easier and faster to perform. Additionally, information about the relaxation behavior and degradation of the PP phase was obtained from TSSR measurements.

Dynamic vulcanization of TPEs based on poly (Epichlorohydrin – co – Ethylene oxide) and polypropylene (PP) was studied by Mauro et al [29]. Unvulcanized and dynamically vulcanized blends of Poly (Epichlorohydrin – co – Ethylene oxide) elastomer and polypropylene have been prepared by melt mixing in an internal mixer. The solvent resistance, morphology, dynamic mechanical and mechanical properties of these blends were studied with special reference to the effect of crosslinking agent content. The swelling behaviour shows that the blends with and without dynamic vulcanization, present excellent resistance to solvents ASTM A, B, C and D at room temperature. Morphology study by SEM of the cryofractured surface and analysis of the dynamic mechanical properties of the system indicate that the uncrosslinked blend is immiscible and form a two phase structure, where the rubber phase was dispersed as domains in the continuous PP
matrix. The mechanical properties of the cross linked blends do not improve by increasing the doses of cross linking agent.

Komalan et al [30] made an insight into the dynamic mechanical analysis of binary and ternary polymer blends based on nylon copolymer/EPDM rubber and EPM grafted maleic anhydride compatibilizer. The dynamic mechanical properties such as storage modulus, loss modulus and damping properties of the blends of nylon copolymer (PA 6, 66) with ethylene propylene diene (EPDM) rubber was investigated with special reference to the effect of blend ratio and compatibilization over a temperature range 100°C to 150°C at different frequencies. The effect of change in the composition of the polymer blends on tanδ was studied to understand the extent of polymer miscibility and damping characteristics. The loss tangent curve of the blends exhibited two transition peaks, corresponding to the glass transition temperature (t_g) of individual components indicating incompatibility of the blend systems. The morphology of the blends has been examined by using scanning electron microscopy. The Arrhenius relationship was used to calculate the activation energy for the glass transition of the blends. Finally, attempts have been made to compare the experimental data with theoretical models.

A survey was made by Sen et al [31] on kinetics of silane grafting and moisture crosslinking of polyethylene and ethylene propylene rubber. Peroxide initiated graft copolymerization of vinyl trimethoxysilane (VTMO) and vinyl triethoxysilane (VTEO) onto polyethylene (PE) and ethylene copolymer (EPR) was studied. The kinetics of grafting, studied by DSC, are the same for all the systems and the activation energy for VTMO is 170 ± 4 kJ/mol. Activation energy for VTEO is 185 ± 5 kJ/mol. The VTMO and VTEO graft copolymers of PE and EPR were prepared by reactive processing in a Brabender Extruder in the temperature range of 150 – 200°C. Moisture catalyzed crosslinking of the silane grafted copolymer was also studied. The influence of the structure of the catalyst, its concentration, moisture concentration, temperature and time on the degree and the rate of crosslinking have been evaluated. Crosslinking reaction follows first order kinetics with respect to both catalyst and moisture concentration. Activation
energy ($E_\alpha$) of the crosslinking reaction has been determined as 65 kJ mol$^{-1}$. The mechanism of grafting and crosslinking are discussed.

2.2. Literature review on TPV using silicone as elastomer:

Gornowicz et al [32] reported a method for preparing a thermoplastic silicone elastomers. The thermoplastic silicone vulcanizate (TPSiV) made according to this invention possesses a significant high tensile strength & elongation at break compared to the simple blend. The silicone polymer used in this invention in a high molecular wt. gum. Even when such gum and specific thermoplastic resin are used to make TPSiV, the authors found that there is a critical range of silicone content over which above mentioned improvement in tensile strength & elongation at break are obtained. In the present invention the TPE is prepared by mixing a thermoplastic resin (a polyolefin or PBT) with a diorganopolysiloxane having plasticity 30 and having at least 2 alkenyl radicals in its molecule – then dynamically curing the silicone with an organohydrides Silicone compound containing at least 2 silicone bonded hydrogen in its molecule and a hydrosilylation catalyst. The dosage of the catalyst two mentioned chemicals i.e., curative system should be sufficient to cure the silicone used. In this invention the amount of silicone used was such that either tensile strength or elongation at break of TPE is at least 25 % higher than respective properly of a corresponding simple blend.

Romenesko et al [33] reported on a fire resistant TPSiV through a patent. They investigated on preparation of a fire resistant TPSiV from a polyolefin (PE or PP), polyorganosiloxane having at least 2 alkenyl radicals per molecule and calcium silicate, having average particle size 2 to 30 micron. Here polyorganosiloxane was dynamically cured using an organohydrido silicone compound containing at least 2 silicone-bonded hydrogen groups per molecule and hydrosilation catalyst. The resultant TPV was found possessing excellent fire resistance characteristics. When this TPSiV was tested by burning at 40 – 88 kW/m$^2$, it not only generated significantly less heat & smoke, but left tougher chars compared to a simple mixture of polyolefin, polyorganosiloxane and calcium silicate where the polyorganosiloxane is not dynamically cured.
A patent on polyolefin thermoplastic silicone elastomers employing radical cure was filed by Chorvath et al [34]. Their research work provided a method for preparing a TPE from a thermoplastic resin, a silicone base and a radical initiator by dynamic vulcanization. First a silicone base was made from:

100 pbw of diorganopolysiloxane gum with a plasticity of at least 30 and having at least 2 alkenyl groups per molecule and up to 200 pbw of a reinforcing filler. TPE was prepared by mixing a thermoplastic polyolefin resin, constituting more than 50 % by volume, silicone base, then dynamically curing the silicone with an organic peroxide. The TPEs obtained have an elongation of at least 25 % and one property either tensile strength or elongation at break is at least 25 % greater than the respective property of the simple blend of the constituents mentioned above where the silicone is not cured.

Combining the benefits of engineering thermoplastic and high performance silicone rubber, TPSiV materials expand the performance scope of resulting TPV. These new materials exhibit thermoplastic behavior during processing and many thermoset rubbers characteristic during end use applications. Their capability of withstanding oils, chemical, temperatures and UV radiation will find them many underhood application in automotive and in certain industrial environment. This high performance of TPV was reported by Gross et al [35].

The preparation of TPEs based on silicone rubber & PE by thermo mechanical reactive blending & the effects of PE structural parameters, on TPE was reported by Katbab et al [36]. Attempts have been made to prepare TPEs based on PE and silicone rubber by thermo mechanical reactive mixing of two polymers. Occurrence of both grafting and vulcanization of silicone rubber chains was evidenced by the increase in the mixing torque, solvent extraction data, as well as FTIR and DSC analysis. Among the different types of PE, LLDPE showed higher potential to promote reactions between the two phases. The blend based on LLDPE prepared at the high temperature and shear rate exhibited distinct rheological behavior with a non-newtonian characteristic and higher dynamic viscosity measured by rheomechanical spectroscopy (RMS) than the two individual components at low frequencies.
Jana et al. [37] studied thermo gravimetric analysis of blends of low-density polyethylene and poly (dimethyl siloxane) rubber and the effect of compatibilizers. The thermal stability of vulcanizates of low-density polyethylene (LDPE), poly (dimethylsiloxane) (PDMS) rubber, and their blends was studied by non-isothermal thermogravimetry. Four ethylene copolymers ethylene methyl acrylate (EMA), ethylene vinyl acetate (EVA), ethylene acrylic acid (EAA), and a zinc-salt-based ionomer (Lotek 4200) were used as compatibilizers for the blend systems.

The thermograms and derivatograms of the blends showed that thermal degradation took place in two stages, whereas those for the base polymers showed single-stage degradation. Kinetic studies of the blends and pure components showed that the degradation followed first-order reaction kinetics. The activation energy at 10% degradation was determined with the Freeman-Carroll method and was at a maximum (42.34 kcal/mol) for the 25:75 LDPE/PDMS rubber blend. The half-life at 200°C was evaluated by the Flynn-Wall method and was at a maximum (812.5 days) for the same blend. Out of four compatibilizers, EMA showed the maximum activation energy (34.25 kcal/mol) for degradation and a maximum half-life (695.3 days), indicating that EMA was the best compatibilizer for the blend system.

In another study Jana et al. [38] reported on compatibilized blends of LDPE and PDMS rubber as effective cable insulants. Blends of low density polyethylene (LDPE) and poly (dimethylsiloxane) rubber (PDMS) compatibilized with ethylene methyl acrylate (EMA) have been found to be effective heat resistant cable insulators. Various electrical, mechanical, and thermal properties have been studied. From these studies, the authors concluded that the blends can be used for heat resistant insulation. It is cost effective compared with silicone rubber based insulation.

Gross et al. [39] studied thermoplastic silicone elastomers from compatibilized polyester resins. Their invention as detailed in patent provides a method of preparation of TPE from a thermoplastic polyester resin with a melting point 23°C to 300°C and which will constitute more than 50% by vol., a silicone
elastomer. As this combination is not compatible with each other, they used a glycidyl ester as compatibilizer. The silicone base was first made from:

100 pbw of diorganosiloxane gum with a plasticity of at least 30 and at least 2 alkenyl groups in its molecule and preferably 20 to 100 pbw of a reinforcing silica with surface area 200 – 380 m²/g. To this, suitable amount of anti-creeping agent was also used. The cross linking system used for dynamic vulcanization of the above mentioned Silicone comprises an organohydrido silicone compound which contains at least 2 silicon-bonded hydrogen in its molecule and hydrosilation catalyst. The weight ratio of silicone to thermoplastic polyester is 35 : 65 to 85 : 15. The subject TPE was prepared by first making a compatibilized blend of thermoplastic polyester resin & silicone – then dynamically curing silicone elastomer using the cross linking system already mentioned. The TPE obtained was found to possess elongation of at least 30 % and one property – either tensile strength or elongation at break at least 25 % higher than the respective property of the simple blend of the constituents, mentioned above where silicone is not cured.

Jana et al [40] attempted to find out the effect of ethylene copolymers as polymeric compatibilizers for LDPE and PDMS rubber blends. The effect of different ethylene copolymers such as ethylene methyl acrylate (EMA), ethylene vinyl acetate (EVA), ethylene acrylic acid (EAA) and an ionomer (Lotek-4200) as compatibilizers for 75:25 blends of low density polyethylene (LDPE) and poly dimethylsiloxane rubber (PDMS) have been studied. The results are based on physicomechanical properties, thermalanalysis, phase morphology, dynamic mechanical properties and x-ray diffraction (XRD) studies. It has been observed that mechanical properties of the blends improve with the incorporation of compatibilizers. A study of lap shear adhesion strength of the blend shows an increase in adhesion strength as the compatibilizer concentration is increased in the system up to a certain level of compatibilizers. Phase morphology studies by scanning electron microscope (SEM), show a reduced domain size (2-5 mm) for the compatibilized blend. Dynamic mechanical analysis also supports the strong interaction of the compatibilizer with the blend constituents. Thermogravimetric
analysis indicates an increase in thermal stability of the blends with the addition of compatibilizers.

Chorvath et al [41] studied method of preparing thermoplastic silicone vulcanizate using nylon resins. Their invention as detailed in patent provides a method of preparation of a TPE from a rheologically stable polyamide resin, silicone base and stabilizer. The wt ratio of silicone base to polyamide resin is from 35:65 to 85:15. The crosslinking system used for dynamic vulcanization of silicone comprises an organohydrido Silicone compound which contains at least 2 silicon-bonded hydrogen in its molecule & a hydrosilation catalyst.

The silicone base was first made by blending uniformly 100 pbw of diorganopolysiloxane gum having plasticity from 120-185 and at least 2 alkenyl radicals in its molecule and preferably 20-100 pbw of fumed silica along with a suitable anti creeping agent.

The subject TPE was prepared by first mixing the polyamide resin, silicone base & stabilizer at a dose of 0.475 – 0.525 pbw per 100 part (by wt.) of PA plus silicone base, then dynamically curing the silicone using the cross linking system already mentioned. The TPE obtained was found having elongation at least 25 % and one property either tensile strength or elongation at break at least 25 % greater than the respective property of the simple blend of the constituents, mentioned above where Silicone is not cured. The authors further observed two important & beneficial effects of incorporating stabilizer in TPE composition

I) enhancement of tensile strength & elongation at break
II) reduction of melt viscosity of TPE which will be very helpful for processing the subject TPE.

Fournier et al [42] studied thermoplastic silicone elastomer from compatibilized thermoplastic polyamide. Their invention provides a method of preparation of a thermoplastic elastomer from a polyamide resin with melting point or glass transition temperature of 25°C to 275°C, a silicone base, a stabilizer and a compatibilizer. The crosslinking system used for dynamic vulcanization of silicone comprises an organohydrido silicone compound containing at least 2 silicon-bonded hydrogen in its molecule and a hydrosilation catalyst. The required silicone base was first made by uniform blending:
100 pbw of a diorganosiloxane gum of plasticity preferably 120 – 185 with 20 – 100 pbw fumed Silica and anti creeping agent.

The weight ratio of Silicone base to polyamide resin is from 40:60 to 70:30. According to the procedure, described in the patent, first a polyamide, silicone base, 0.475 – 0.525 pbw of stabilizer (per 100 part of PA plus silicone base) and compatibilizer (0.2 – 3 pbw for 100 parts of PA resin) was thoroughly mixed above the melting temperature of PA resin and dynamically curing the silicone by incorporating the cross linking system in an amount sufficient to cure diorganopolysiloxane. One property – either tensile strength or elongation at break of the TPE obtained was found at least 25 % higher than the respective property for a corresponding simple blend in which silicone is not cured.

Naskar et al [43] reported mechanical properties of TPEs based on silicone rubber and ethylene-octene copolymer by dynamic vulcanization. TPVs are a special class of TPEs that are generally produced by the simultaneous mixing and crosslinking of a rubber with a thermoplastic polymer at an elevated temperature. Novel peroxide-cured TPVs based on blends of silicone rubber and thermoplastic Engage (an ethylene-octene copolymer) have been developed. These TPVs exhibit very good overall mechanical and electrical properties. With an increasing concentration of DCP, the tensile strength, modulus and hardness of the TPVs increase, whereas the elongation at break decreases. Significant-correlations have been obtained from Oscillating Disc Rheometer torque values with various physical properties, such as the modulus and tension set of the TPVs. The aging characteristics and recyclability of the silicone-based TPVs are also excellent. SEM, photomicrographs of the TPVs have confirmed a dispersed phase morphology.

Basuli et al [44] reported TPVs based on blends of silicone rubber and Engage- olefinic thermoplastics. These TPVs exhibit very good overall mechanical properties with respect to two different types of Engage (Engage-8440 and Engage-7256). With increasing amount of Engage in the blends at a fixed DCP concentration of 2.5 phr, tensile strength elongation at break, modulus and hardness of the TPVs were found to increase considerably. This can be explained by the incorporation of more thermoplastic hard component in TPVs. Ageing
characteristic and recyclability of these TPVs are also found very good. Peroxide cured silicone rubber/Engage TPVs exhibit very good overall performance towards heat ageing resistance, processability and recyclability. PDMS/Engage-8440 system was compared with PDMS/Engage-7256 system for physical properties, heat aging, processability, and morphology studies. PDMS/Engage-8440 system was found to exhibit better behavior in all respect. Rheological studies also confirm the pseudo plastic nature of these TPVs.
2.3. References:


[34] Igor Chorvath, Dean Curtis Gray, Michal Kang-Jen Lee and Thomas John Tangney US Patent 6479580 B1, Date – Nov. 12, 2002.


Scope and Objective of the work:

It was evident from literature review that the works done till date, are mostly concerned with PP-EPDM system which has found wide commercial applications also. Though silicone rubber is considered as a very specialty polymer, but in this modern era, one will hardly find an area/field (in Industry, medical use & personal care) where silicone does not find any application. Compared to major used organic elastomers – silicone has many unusual properties. They are characterized in particular by

- High thermal stability,
- Physical properties which are largely independent of temperature,
- Physiological compatibility,
- Good dielectric properties,
- High resistance to radiation especially to UV light,
- Excellent hydrophobicity & hydrophobicity recovery characteristic.

Besides these unique combinations of different properties, silicone offers flexibility of processing & also freedom of product design.

These properties are exploited in many critical and very important applications in various industries. Because of its very high price, it is used mainly in the high end variety of different products. Considering the versatility of silicone rubber in diversified application and the scope of incorporation of the processing advantages of thermoplastic materials – along with an objective to lighten the price burden – systematic endeavors have been made to synthesize innovative “thermoplastic silicone elastomer”.

In this work, use of silicone in a very critical & important electrical application, (more specifically in electric power transmission & distribution) has been considered. In electric power transmission & distribution, composite insulator is a new generation product which offers many technical advantages over the age old conventional ceramic insulators specially in polluted environment. Long term uninterrupted performance of composite insulator depends on quality of silicone housing. This compound should have a well balanced combination of mechanical, electrical & weather resistance characteristics. Besides being a good dielectric material, the desired polymeric compound should possess very high
level of track resistance, excellent hydrophobicity & hydrophobicity recovery characteristic in case of its loss by any means.

Keeping the nature of application in mind, a very specialty POT (Polyolefin Thermoplastic) was selected as the plastomeric component along with the major component of silicone elastomer for the synthesis of the subject TPSiE. Its selection has been made in a manner such that the resultant TPV is not only as soft & flexible as silicone rubber, but also it can be quite useful in terms of acceptability of high dose of some specialty fillers resulting in a unique highly filled but flexible TPV.

Because of peculiar structural features, silicone is incompatible with major macro molecules. Technological compatibilization between the constituent elastomer & thermoplastic is very much required to have useful technical properties & smooth processing characteristic from the TPV.

So in broader sense, the primary object of this work is to study the synthesis of thermoplastic silicone elastomer – first in unfilled stage, then to incorporate high dose of specialty filler to bring the desired properties along with the ease of processing characteristic typical of thermoplastics.

Among various methods of compatibilization, in this work reactive compatibilization method is adopted for making a compatibilized blend of silicone & POT.

The entire work is divided into four parts. In the first & second part, two different routes are explored to make a compatible blend of silicone & POT. In two routes two different compatibilizers are tried & optimization of compatibilizer level is done. As the objective is to synthesis a TPV, where the elastomer will exists as micronized particles dispersed in a minor thermoplastic matrix, level of curative & shear rate employed during dynamic vulcanization are also equally important. After determination of the optimum level of compatibilizer in the uncrosslinked blend, study was undertaken to assess the effect of dynamic vulcanization carried out at varying doses of curative at a fixed shear rate to find out the optimum level of curative. In the next step dynamic vulcanization was carried out using the composition containing the optimum curative dose, at varying shear rate thereby finding out the optimum level of shear rate. In the third
part, a TPV was synthesized from silicone rubber & EMA. Here EMA played a dual role – compatibilizer cum thermoplastic part of the TPV matrix. Two types of silicone – differing in mole percent of vinyl were used with EMA separately to study the effect of vinyl group of silicone in the resulting TPVs. TPVs obtained at different stages were characterized for various mechanical properties to select the best TPV from the respective systems. Thermal, electrical, rheological, ageing, morphology, recycling characterizations were also carried out with the TPVs.

The fourth part of the dissertation is concerned with filled TPV system using the best unfilled TPV (obtained from part I & part II) along with a specialty filler. Work on filled system was targeted for development of a highly track resistance, dielectric polymer compound with unique hydrophobicity recovery character for outdoor electrical application.