1.1 Introduction

The field of materials research and their applications during the last few decades has been revolutionized by polymer blends and alloys. Polymer blending is an attractive method of creating new materials obtained by the combination of two or more structurally different polymers or copolymers giving rise to certain range of properties, not delivered by any of the constituents. Furthermore, synthesizing new polymer is time consuming and involves significant costs (Shonaike and Simon 1999; Utracki, 1989). The production of polymer blends by means of melt-mixing technologies presents a well–established and cost effective way for the development of new polymeric materials. A vast majority of polymer blends are immiscible due to small entropy of mixing for very large molecules. Miscibility depends of molecular structure, blend composition and mixing temperature. Before proceeding it is necessary to clarify the terms miscibility and compatibility (Paul and Newman, 1978). Miscibility refers to the polymer mixture with adequate molecular level of mixing to yield macroscopic properties expected to that of a single phase. On the other hand, compatibility is often used to describe a good adhesion between blend constituents with heterogenous phase structure. An understanding of polymer blend miscibility and/or compatibility is important, both for understanding the melt state processing and manipulating the properties of final product. For the successful development of a blend, the control of the complex correlations between the thermodynamic interactions, forces affecting the polymer components as well as the process parameters are of fundamental importance (Paul and Bucknall, 2000). Figure1.1 shows the schematic representation of complex interrelationship between the properties and parameters involved in the selection of polymer blends. The design and development of the polymer blend system strongly depends on two major parameters; the control of the interface and the control of the morphology. The morphology of the polymer blend indicates the size, shape and spatial distribution of the component phases with respect to each other. It is well established that most of the properties like mechanical, optical, barrier and rheological properties are strongly influenced by the type and fineness of the phase structure. When two immiscible polymers are mixed, the size, shape and distribution of one phase into the other depends on the material parameters (such as blend composition, viscosity ratio, elasticity ratio and interfacial interaction) as well as

processing conditions (such as temperature, time, intensity of mixing and nature of flow) (Harrats *et al*., 2006).
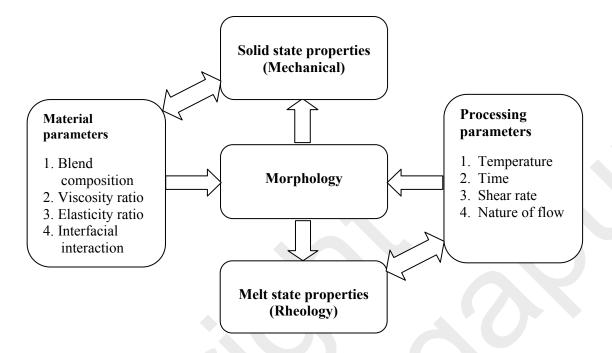

Figure 1.1: Schematic Representation of Relationship between Mechanical, Morphology and Rheology of Polymer Blends

1.2 Polymer blends

Polyolefin blends are a subset of polymer blends, which are formulated to broaden the range of structures, properties and applications offered by polyolefins (Nwabunma and Kyu, 2008). Polyolefin blends are generally immiscible due to hydrophobic or nonpolar nature of polyolefins. Immiscibility of polyolefin blends can be mitigated by using compatibilizer and/or reactive processing. Technologically compatible blends are those which are immiscible from the thermodynamic point of view, but are made to appear as miscible ones from technological basis and their applications from commercial point of view. These mixtures are homogenous in macro scale but remain heterogeneous in the micro scale (Solc, 1982).

1.3 Polyolefin rubber/plastic blends

A large number of rubber-plastic blends exists from the wide range of polymers available in market. Although numerous rubber-plastic blends are available, only few of them are commercially attractive because of compatibility between the components (De and Bhowmick, 1990). In general, rubber-plastic blends can be broadly classified into two categories: rubber toughened plastics and thermoplastic elastomers (TPEs). Most of the commercially important plastics such as polypropylene, polystyrene, polycarbonate, and polyamide lack in good impact resistance. This can be improved by addition of small amount of rubbery material, compatible with the plastic phase. For example, ethylene propylene diene rubber (EPDM) is often blended with polypropylene (PP) to increase its impact strength. On the other hand, TPEs can be defined as a class of polymers, which combine the service properties of elastomers with the processing properties of thermoplastics. Therefore TPEs bridge the gap between conventional rubbers and thermoplastics. They provide the simplest way of achieving outstanding properties at low cost having the scope to achieve tailor-made properties by simple variation of the blend compositions, viscosity of the components and compounding ingredients (Legge and Holden, 1987). The development of various TPEs has been reviewed in many literatures (De and Bhowmick, 1990; Legge and Holden, 1987; Bhowmick and Stephens, 2001). The field of TPEs based on polyolefin rubber/ thermoplastic compositions, has grown along two distinctly different product-lines or classes; one class consists of simple blends and is commonly designated as thermoplastic elastomeric olefins (TEOs) or thermoplastic olefins (TPOs). In the other class, the rubber phase is dynamically vulcanized, giving rise to a thermoplastic vulcanizate (TPV).

TEOs are simple blend of rubber and plastic, exist as multiphase materials. Their useful level of strength can be retained upto the softening point of the highest melting continuous phase component. However TEOs have not replaced the thermoset rubber since they do not provide sufficient resistance to compression or tension set particularly at elevated temperature or under prolonged deformation. Furthermore, TEOs swell to a higher extent when exposed to solvents due to the existence of non-crosslinked amorphous rubber (Bhowmick and Stephens, 2001).

TPVs, are produced by dynamic vulcanization of immiscible blends of rubber and thermoplastic, i.e., selectively crosslinking the rubber phase while mixing with the thermoplastic at elevated temperature. If the crosslinked rubber particle of such blends are small enough and if they are fully vulcanized then the following properties are greatly improved:

1. Reduced permanent set
2. Improved ultimate mechanical properties
3. Improved fatigue resistance
4. Greater resistance to fluids e.g., hot oils
5. Improved high temperature utility
6. Greater stability to phase morphology in the melt
7. Greater melt strength

In short, dynamically vulcanized blends can provide compositions, which are very elastomeric in their performance characteristics (Shonaike and Simon, 1999).

1.4 Concept of dynamic vulcanization

Thermoplastic vulcanizate (TPV) were first introduced in 1962 by Gessler and Haslett (1962). TPV is prepared by dynamic vulcanization process that involves the crosslinking of a rubber phase while it is being mixed with a thermoplastic to form a homogenous melt. The process needs to be carried out under high shear and above the melting temperature of the thermoplastic component and at sufficient high temperature to activate and to pursue the process of vulcanization (Shonaike and Simon, 1999). As a result, products are obtained which consist of crosslinked rubber particles dispersed in a continuous thermoplastic matrix, that explains both elasticity and melt processability (Naskar, 2004). Earlier work of Fisher (1973) in PP/EPDM TPVs with peroxide as crosslinking agent resulted in the commercialization of "Uniroyal TPR" thermoplastic rubber. Greater industrial attention was generated only after extensive study of TPVs based on various blend components by Coran and Patel in 1980's (1980, 1981, 1982a, 1982b). They performed extensive study on PP and EPDM blends which were dynamically vulcanized with high crosslink density in the rubber phase. This work led to the commercialization for "Santoprene" TPE introduced by Monsonto in 1981. A recent

survey indicates that the global annual growth rate of TPE based on thermoplastic vulcanizates is about 15%. Now TPVs are widely used in automobiles, wires/cables, biomedical and soft-touch applications etc. In principle, a large number of rubber/plastic TPVs are possible and this number is increasing day by day with the introduction of new polymers. But technologically useful blends can only be obtained by the close match of surface energies of the blend components.

1.4.1 Morphology

The evolution of morphology in TPVs is governed by several parameters, including blend composition, viscosity ratio, shear force and interfacial interaction between the two phases (Sengupta, 2004). Initially, with the addition of curative, viscosity ratio plays a major role in the morphology evolution (less viscous phase encapsulate the more viscous phase). With further increase in curative dosage, degree of crosslinking increases in the dispersed phase, although there is an abrupt increase in viscosity ratio resulting decrease in particle size. It is expected that applied shear fields override the viscosity ratio factor. It is further clarified as, enough crosslinking in the rubber phase causes an immobilization of the particles and therefore they break down to smaller particles under the applied shear. The development of the dispersed phase morphology from the co-continuous phase is depicted in Figure 1.2.
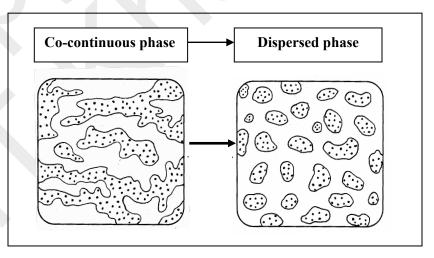

Figure 1.2: Development of Morphology in a Thermoplastic Vulcanizate: from Co-continuous to Dispersed phase

It is generally accepted that one of the major advantages of the dynamically crosslinked blends over unvulcanized blends is that the morphology is fixed on crosslinking and is not altered by subsequent melt processing. Abdou-Sabet and Patel (1991) and later Radusch and Pham (1996) studied the morphology generation during the process of dynamic vulcanization for phenolic resin cured PP/EPDM TPVs. D′orazio *et al*. (1994) studied the morphology of dynamically peroxide vulcanized isotactic polypropylene (iPP)/ ethylene propylene rubber (EPM) by means of differential scanning calorimeter (DSC), by optical, scanning electron microscopy (SEM), transmission electron microscopy (TEM), wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS). Sengupta and Noordermeer (2005) reported the first use of electron tomography in reconstructing the three-dimensional morphology in thermoplastic elastomer blends.

1.4.2 Rheology

Goettler *et al*. (1982) was the first to study the technical importance of the TPVs in terms of rheological characteristics using a capillary rheometer. Han and White (1995) described the comparative rheological study of PP, PP/EPDM uncrosslinked and dynamically crosslinked blends using various rheological instruments to measure steady shear flow, uniaxial extension and oscillation flow properties of the compounds. Steemean and Zoetelief (2000) reported that TPVs have a yield stress for flow and the value increases with increase in elastomer component in TPVs. An extensive study of rheological response of PP/EPDM blends and the TPVs with phenolic resin as curing agent was explored by Jain *et al*. (2000). Katbab *et al*. (2000, 2004) discussed the formation of morphology and correlated with the mechanical and rheological properties for the non-reinforced and reinforced (carbon black and silica fillers) TPVs. Chatterjee and Naskar (2008) analyzed the rheological responses of nano-silica filled PP based TPVs. Rheological behavior of dynamically and statically vulcanized blends of PP and styrene butadiene styrene triblock copolymer (SBS) with reference to the effect of various curing agents was studied by Ichazo *et al*.(2004). The linear viscoelastic properties of PP/styrene-ethylene butylenes-styrene block copolymer (SEBS) blends and PP/EPDM TPVs are described in terms of composition ratio and also discussed about the

oil diffusion and distribution in the blend components by Sengers *et al.* (2004). Recently, Leblanc (2006) studied the nonlinear viscoelastic property of the various commercially available TPVs with varying hardness by a Fourier transform rheometer (FT-rheo) to get insight into the morphology developed and the subtle role played by the extractible content such as oil and plasticizers. The morphology of the TPVs plays a key role in governing the mechanical properties, but its effect is still not well understood.

1.4.3 Deformation behavior

The crosslinking of the rubber phase in PP/EPDM blends results in better rubber-like properties. Analyses during tensile testing of the TPV (Boyce, 2001a, 2001b) and finite element modeling (FEM) (Soliman, 1999; Oderkerk, 2002a,2002b) showed that during deformation in the solid state the PP phase only yields partially. The thin PP films get yielded in the equatorial region (perpendicular to the load applied) of the elastomer particles and the rest of the PP phase remains unaffected. Soliman *et al.* (1999) studied the deformation mechanism of phenolic resin cured PP/EPDM TPV. According to them, during the stretching process of PP/EPDM TPV most of the PP acts as glue between the EPDM particles, which are deformed. Only a small fraction of the PP is irreversibly deformed: yielded. During the recovery process this PP fraction is partially pulled back by the recovery of the EPDM. Oderkerk *et al.* (2002a) studied about the micromechanical deformation and strain recovery process of nylon6/EPDM TPVs by using atomic force microscopy (AFM) and transmission electron microscopy (TEM). Schematic representation of the deformation and recovery of the dynamically vulcanized PP/EPDM blend is shown in Figure 1.3.
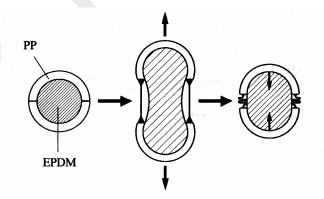

Figure 1.3: Sketch Illustrating the Deformation Mechanism of PP/EPDM TPVs

1.4.4 Production and processing

Thermoplastic vulcanizates based on PP/EPDM are produced using either batch or continuous mixing techniques. The most common batch mixers are internal mixers, such as the Banbury mixers, Barbendar plasticoder, etc. On an industrial scale TPVs are typically produced on twin screw extruders, allowing a large degree of process flexibility. Till recently, the dynamic vulcanization processes were not entirely satisfactory for making soft compositions because as the rubber level rises, the resulting composition become less processable. For example, the compositions give poor extrudates and sometimes, cannot be extruded at all. The fabrication method and equipment (Shonaike and Simon, 1999; Naskar, 2007) for TPVs are essentially those of the thermoplastic in the material. Thermoplastic injection molding does not involve vulcanization, so short cycle time, easy control over processing defects. Extrusion is widely used to fabricate intricate profiles, tubings, hose and electrical insulation and jacketing from TPVs. Blow molding, thermoforming and heat welding can also be done for TPV based materials. Unlike thermoset rubber, generation of hollow articles via blow molding has been found. However, it is generally advisable to dry a TPV prior to processing to avoid process defects.

1.5 Factors affecting the properties

1.5.1 Compatibility

A wide variety of commercially available rubbers and plastics can be considered for blending. However, only a limited number of blends are having technological and commercial importance, since most polymers are incompatible from a thermodynamic sense. Therefore, the selected polymeric materials should be more or nearly compatible to form fine heterophase morphology. This is best illustrated with the blends of PP and EPDM. Grossly, incompatible polymeric blends do not provide sufficient performance properties since they appear inhomogenous systems. In such cases, compatibilizer must be either added or generated *in-situ* to affect apparent homogenation prior to the onset of dynamic vulcanization. An example of this is the blends of nitrile rubber (NBR) and PP. Coran and Patel (1983a) showed that, *in-situ* formation of block copolymer by reactive

amine terminated-NBR and maleic anhydride-PP (MAH-PP) as compatbilizer, could control the morphology of the NBR/PP blend. These *in-situ* formed block copolymers act as macro-molecular surfactants to promote and stabilize the emulsion of the molten homopolymers. Furthermore, it has been found that a dimethylol phenolic resin compound (such as phenolic curative) can be used to technologically compatilize PP and NBR blends (Coran and Patel, 1983b).

1.5.2 Type of curatives

Several crosslinking agents have been employed to crosslink the rubber phase: sulphur, co-agent assisted organic peroxides, activated phenol-formaldehyde resins (commonly known as resol resins), platinum catalysed hydrosiloxane, vinyltrialkoxysilane/moisture, catalysed quinonedioxime and bisthiols (Van duin, 2006). Selection of curatives not only depends on the type of rubber used but also on the thermoplastic component to be used. In dynamic vulcanization, the first curative used was zinc oxide with halobutyl rubber by Gessler (1962). Fisher (1973) controlled the degree of cure by limiting the amount of peroxide. Coran *et al*. (1980, 1981, 1982) employed sulphur vulcanization for a majority of their experiments. However, PP/EPDM based TPVs are traditionally cross-linked with acid-activated resols (Van Duin, 2006). The reaction mechanism of resol curing of ENB-containing EPDM was extensively investigated by Van Duin and co-workers by using 2-ethylidene norbornane (ENBH) as a low molecular weight model compound. Abdou-Sabet *et al.* (1996) demonstrated that the rubber-like properties of PP/EPDM or PP/NBR TPVs could be further improved by using dimethylol-octyl phenol curing resin. They observed tremendous improvements in compression set, oil resistance and processing characteristics of the material. These improvements were beyond those expected from the state of cure, and are probably due to *in-situ* formation of a block copolymer between the rubber and PP. The graft copolymer was assumed to be generated through the functionalization of PP with dimethylol-octyl phenol, which then reacts with the rubber like EPDM or NBR. Phenolic resin curatives having a majority of dibenzyl-ether linkages were unexpectedly found to be effective in curing the rubber in a blend of a crystalline polyolefin and EPDM (Medsker *et al*. 1998). Their effectiveness exceeds that of conventional phenolic resins

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for many TPV compositions. But because of the consequent dark brownish color and the formation of black specks in those TPVs, other cross-linking systems have been explored, such as platinum-catalysed hydrosilane and peroxide/coagent. Recently, Lopez Manchado and Kenny (2001a) employed a special crosslinking agent like benzene-1,3-bis(sulfonyl)azide for the preparation of TPV. They concluded that the sulfonyl-azide group can act as an effective crosslinking agent for the elastomeric phase and can couple the elastomeric with the thermoplastic phase. The cure rate, the final crosslink density, the thermal stability of the crosslinks formed, the safety, health and environmental characteristics of the chemicals used and the costs of the products are all relevant parameters for the final choice of the crosslinking system. The use of peroxide, on the other hand, with polyolefin as the plastic phase, leads to undesirable side reactions because of free radicals that are generated. In case of polyethylene (PE) peroxy radicals lead to crosslinking, whereas in polypropylene (PP) undergo chain-scission (Manfred *et al.,* 2002). The degradation of PP leads to loss of final mechanical properties.

Naskar and Noordermeer (2003) studied the influence the different peroxides on the PP/EPDM TPVs at a fixed as well as varied blend ratios. The three main parameters which primarily govern the final mechanical properties of the TPVs are: the solubility parameter of peroxide relative to the polymers (PP and EPDM), the decomposition mechanism of the peroxide and the kinetic aspects of the peroxide fragmentation. The closer the solubility parameter of the peroxide to that of the EPDM, the higher is the tensile strength and the better is the compression set property. Amongst various peroxide taken for the investigation, dicumyl peroxide was found to show overall best balance of physico-mechanical and elastic recovery properties.

Further to explore the peroxide crosslinking system in PP/EPDM blends, multifunctional peroxides (having coagnet functionality in addition to a peroxide group) were developed to overcome the commonly employed peroxides. Commonly used peroxides generally produce volatile decomposition products, which provide an unpleasant smell or can show a blooming effect. Particularly, 2,4-diallyloxy-6-tert-butylperoxy-1,3,5-triazine (DTBT), a multifunctional peroxide turns out to be a good alternative for the DCP/TAC combination. DTBT has a solubility parameter on the high

side of the spectrum, which directs this peroxide and co-agent combination preferentially to the EPDM-phase during mixing. Moreover, the multifunctional peroxides investigated do provide by-products after their decomposition, but without an unpleasant smell, unlike in DCP. There are several patents describing hydrosilane in presence of a catalyst as a curative for the preparation of TPVs (Umpleby, 1989; Quirk and Kanner, 1987). PP/EPDM blends can also be crosslinked by silane grafting in presence of a small amount of peroxide. Anderlik and Fritz (1992) investigated the tension set and repeated stress-strain properties to characterize the elastic properties of organosilane crosslinked PP/EPDM TPV. Grafting, hydrolysis and condensation crosslinking reactions were carried out in a single stage process.

1.5.3 Degree of cure

Attainment of proper crosslink density is required to achieve optimum physical properties. The crosslink density of the rubber phase influences the stress- strain properties of the TPVs, especially at strain larger than 100%. The elastic recovery of the blends is significantly influenced by the crosslink density of the rubber phase, even though the particles are separated by a thermoplastic matrix phase. Partially crosslinked TPVs show inferior tensile strength, tension set, oil resistant, elongation at break, etc., than fully crosslinked blends. Coran *et al*. demonstrated the beneficial effects of high degree of vulcanization (Al-Malaika, 1997). Generally crosslink density can be determined by solvent swelling method using Flory-Rehner equation. Ellul (1995) described the use of solid state NMR spectroscopy to estimate the crosslink density.

1.5.4 Effect of additives

Fillers, oils and plasticizers can be added to TPVs to obtain the desired change in properties. The addition of oils and plasticizers allow the preparation of softer compositions that lead to significant improvements in processability and elastic recovery. In the melt state, oil participates in lowering the viscosity of the plastic phase and expands the solid crosslinked rubber phase, resulting in very good injection molding and extrusion in subsequent steps. On crystallization oil is believed to be absorbed by the amorphous rubber phase and is not rejected on the surface. Undoubtedly some of the oil

resides at the amorphous region of the plastic phase, thus improving the elasticity of the blend. A novel approach to study the oil distribution has been proposed by Sengers *et al.* (2003). They used dielectric relaxation spectroscopy (DRS) to determine the oil distribution in the solid state. The oil distribution in the melt was measured by comparing the storage and loss moduli of ternary blends with those of binary PP-oil and vulcanized EPDM – oil blends and making use of empirical models. Results showed that in the solid and in the melt state, oil prefers the elastomer phase. In general, antioxidants are added to increase the service life. The most commonly employed antioxidants in TPVs are the primary antioxidants like amines and hindered phenols (e.g., Irganox® 1076). They are also called 'chain stoppers", because they stop the free-radical chain reaction of oxidation. Conversely, thio-compounds or phosphites (e.g., Irgafos® 168), known as secondary antioxidants. They basically decompose hydroperoxides and thereby stop the propagation of the radicals by forming stable products. Phosphites show strong synergistic effects in combination with phenolic antioxidants and thus are very frequently used in TPV-compounds (Naskar *et al.,* 2004).

Different types of reinforcing (mostly carbon black and silica) and non-reinforcing fillers (mainly to reduce the cost) are used in TPV formulations (White *et al.*, 2009). They are mainly intended to increase the final physical properties and also to reduce the cost. The added fillers mostly tend to stay in the rubber phase. Recently, some suitable halogen free mineral fillers include aluminum trihydroxide, magnesium dihydroxide, ammonium phosphate, diammonium hydrogen phosphate, polyammonium phosphate, and tribromoneopentyl esters of phosphoric acids etc., are used. On the other hand, examples of fire-retardant fillers are halogenated fire-retardant agents such as chlorinated biphenyl and halogenated cyctopentadiene used jointly with metal oxides such as antimony oxide, halogenated polymers, mixtures of halogen and phosphorus fire-retardants etc. Examples of some sound dampening mineral fillers include magnesium sulfate, calcium sulfate, barium sulfate, aluminum sulfate, aluminum ammonium sulfate, aluminum potassium sulfate, aluminum sodium sulfate, magnesium carbonate, calcium carbonate, calcinated clay, calcium borate, talc, mica, zinc borates, and aluminum phosphate etc. Very recently, different types of nano-sized mineral fillers like nano-clays,

nano-talc etc. are also being used to prepare nano-TPVs (Lee and Goettler, 2004; Naderi 2007).

1.6 Thermoplastic vulcanizates based on polyolefin blends: An overview

Early work of Fisher (1973) on PP/EPDM resulted in the commercialization of "Uniroyal of TPR" thermoplastic rubber in 1973, first commercially utilized blends, prepared by partial crosslinking of rubber phase by peroxide. He basically limited the concentration of peroxide, since peroxide degrades the PP during mixing. Coran and Patel (1980, 1981, 1982) made significant contribution over previous polyolefin blends to produce high quality TPEs, by the process called dynamic vulcanization having high crosslink density in the rubber phase. This work leads to the commercialization of "Santoprene" introduced by Monsanto in 1981. According to Abou- Sabet *et al*. (1996), use of dimethylol octyl phenolic curing resin for TPVs gave improved compression set, oil resistant and high elasticity and also improved processing characteristics. Dynamically vulcanized blends based on phenolic resin (Santoprene) is preferred and commercialized due to good high temperature property, whereas sulphur curatives are not applied commercially, because sulphur lacks in thermal and UV stability, moreover suffers in production problems.

TPVs based on PP and EPDM were extensively studied in the last two decades, and to a lesser extent those based on butyl rubber/PP, natural rubber/PP, and nitrile rubber/PP. Earlier work of De and coworkers (De and Bhowmick, 1990; Kuriakose, 1985a, 1985b,1986; Akhtar, 1985, 1987; Thomas, 1986) involved in the development of natural rubber (NR) based TPVs such as PP/NR, PE/NR, EVA/NR/PP using various types of crosslinking system. Recently, Nakason *et al.* (2005, 2006a, 2006b, 2006c, 2008) reported the effect of graft copolymer on both PP and NR such as maleic anhydride modified PP (Ma-g-PP), phenolic modified PP (Ph-g-PP) on the properties of TPVs with epoxidized NR and maleated NR using sulphur, , peroxide and multifunctional peroxide crosslinking system. Thomas and co-workers (Mathew, 2000, 2001; George, 1999, 2000a; Moly, 2002; Asaletha, 1998; Kumar, 2003) extensively involved in the development of various rubber plastic blends in means to prepare TPEs and TPVs for special purpose application. A large number of research articles are available based on

the structure-property relationship of PP/EPDM TPVs (Ellul, 2004; Van Duin, 2005; Jain, 2000,2002; Gupta, 2000; Goharpey 2004,2007, 2008; Verbois, 2004; Shen, 2007; Tsai, 2008; Wright, 2001; Tang, 2004; Maiti, 2006; Abdel-Barg, 1999). Radusch and Pham (2006) reported that the softer EPDM/PP TPVs have outstanding resistance to flex fatigue, indicating fatigue resistance superior to those of thermoset rubbers. In general compression set and fatigue life are mutually exclusive, understood readily in terms of vulcanization chemistry. But PP/EPDM gives both low compression set and outstanding resistance to fatigue life. Their resistance to aqueous media (acids, alkalis, salt solution) is excellent. Resistance of EPDM/PP TPV to hydrocarbon media is quite comparable to that of neoprene rubber. The most deleterious fluids to these TPVs are halocarbon and highly corrosive media such as fuming sulphuric acid. Anderlik and Fritz (1992) studied the elastic properties of organosilane crosslinked PP/EPDM TPV. Grafting, hydrolysis and condensation crosslinking reaction are carried out in a single stage process.

Very recently Naskar (2007) reviewed extensively on the thermoplastic elastomers based on PP-EPDM blends prepared by dynamic vulcanization. Van Duin (2006) also reviewed critically the recent developments in PP/EPDM TPVs as well as on some technological highlights. A whole range of grades of varying hardnesses is made available by changing the PP/EPDM ratio and adding an extender oil. Commercially available PP/EPDM TPVs are produced by Advanced Elastomer Systems (AES): Santoprene; DSM Thermoplastic Elastomers: Sarlink; Softer Sp A: Forprene; Himont:Dutralene; Mitsui: Milastomer, etc.

1.7 Peroxide as crosslinking agents

Sulphur has been used since the early 1800's for the vulcanization of rubber. Peroxides, on the other hand have been used for vulcanization since the mid 1900s. In 1914, Ostromyslenski, a Russian researcher was the first to discover that natural rubber could be transferred into a crosslinked state after treatment with dibenzoyl peroxide. However, serious interest in vulcanization with various peroxides commenced only with the commercial introduction of dicumyl peroxide (DCP) by Hercules in the late 1950s. DCP was the first commercially available peroxide to combine high efficiency, good vulcanizate properties with low cost and broad spectrum utilities (Naskar, 2007).

Peroxides interact with polymers in a variety of ways, initiate polymerization, modify their rheological properties (vis-breaking), alter polarity or attach functional groups (grafting) and enhance high temperature performance (vulcanization). The effect that peroxide has on a polymer depends on the nature of the polymer type and concentration of the peroxide, reactivity of other component present (Dluzneski, 2001). The driving force of peroxide vulcanization is free-radicals. Radicals are atoms or molecular fragments that contain an unpaired electron. These unstable radicals energetically react in ways that allow the electron to pair with another. Although all radicals are unstable, some are more reactive than others. The major advantages of using peroxide crosslinking system are (Sanchez and Myers, 2006):

1. Improved high temperature resistance
2. Reduced compression set
3. Ability to crosslink saturated as well as unsaturated rubber
4. Rapid vulcanization without reversion
5. Formation of C-C bond, which is similar to the bond strength to every other bond in polymer backbone

The basic peroxide crosslinking reaction consists of three main steps as shown in Figure 1.4. In this process, thermal energy causes the homolytic cleavage of the peroxide molecule to create radicals. These radicals then abstract hydrogen from the polymer to form polymer radical. Eventually two polymer radicals combine to form a covalent crosslink (Dluzneski, 2001). In addition to the above productive reactions, numerous side reactions may take place during the course of the reaction (Akzo-Nobel, Technical bulletin), which reduces the efficiency as shown in Figure 1.4. Peroxide crosslinking needs special attention system for the selection of compounding ingredients, material such as plasticizers, oils and acidic fillers (such as silica) otherwise it might affect the crosslinking efficiency.

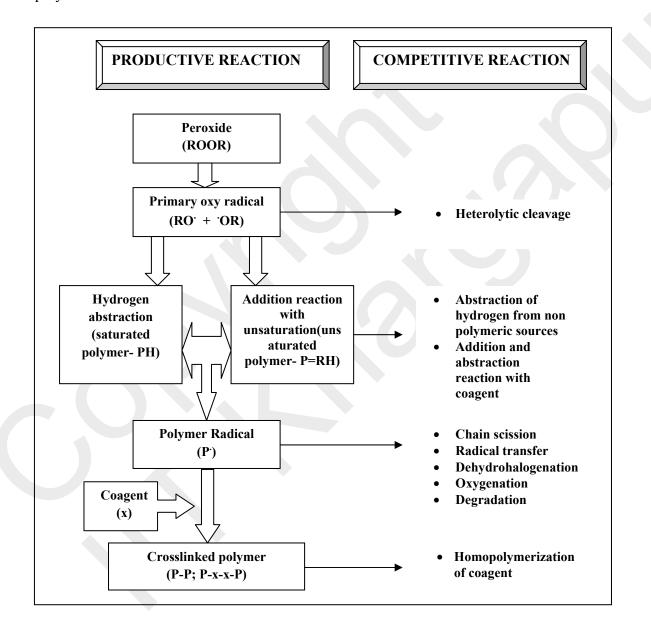*Criteria for the selection of peroxide*:

The following are the some of the important criteria in selecting peroxide (Geo Specialty Chemicals, Technical bulletin)

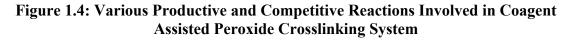 1. It should be efficient in vulcanizing the elastomer

2. The decomposition temperature should be moderate to have scorch safety and fast cure rate

3. It should not be vulnerable to side reaction, which reduces the efficiency

4. It should be non-volatile, non-toxic and non-irritating

5. Neither the peroxide nor its decomposition products should cause degradation of the polymer

Figure 1.4: Various Productive and Competitive Reactions Involved in Coagent Assisted Peroxide Crosslinking System

In order to get desired property and process safety during vulcanization, it is necessary to select a proper peroxide. To choose the most suitable peroxide for vulcanization purpose, it is necessary to know the characteristics of the peroxide. The following are the most important characteristics of peroxide.

Active oxygen content: Active oxygen content represents not only the amount of free radicals produced from the peroxide, but also the concentration and purity of peroxide. Peroxide with low active oxygen content is less efficient in vulcanization, simply because the peroxide group is more dilute on a molecular level.

Half life period: Half life period is defined as the time required for the decomposition of one half of a given quantity of a peroxide in dilute solution at a given temperature. Decomposition is a first order reaction and characterized by the given temperature. For convenience to compare the stability of peroxides in dilute solutions, they are commonly listed accordingly to the temperature at which they have half lives of 10 hrs or 1 hr. Commonly, the half life time is determined by the differential scanning calorimetric-thermal activity monitoring (DSC-TAM) of a dilute solution of the peroxide in monochlorobenzene. The dependence of the half-life time on temperature can theoretically be described by the Arrhenius equation.

$$k_d = A.e^{-\frac{E_a}{RT}} \qquad \text{------------ (1.1)}$$

$$t_{1/2} = \frac{\ln 2}{k_d} \qquad \text{------------ (1.2)}$$

where

k_d = rate constant for the peroxide decomposition(s^{-1})
A = Arrhenius frequency factor(s^{-1})
Ea = activation energy for the peroxide decomposition (J/mol)
R = 8.3142, gas constant,(J/mol.K)
T = temperature (K)
$t_{1/2}$ = half-life time(min)

Activation energy: Activation energy is defined as the energy required to activate the decomposition mechanism. Although all peroxides are thermally viable to decompose to yield free radicals, but their relative stabilities vary considerably. Volatility is also an important determinant in shelf-life and transportation. Most stable peroxide includes dialkyl, diaryl and diaralkyl types, whereas the peroxy esters possess only a limited thermal stability.
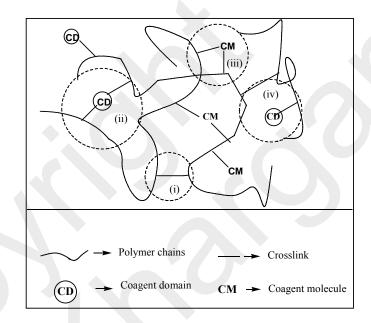
1.8 Coagents for peroxide crosslinking

Coagents are multifunctional vinyl monomers, which are highly reactive towards free radicals. Since all the co-agents contain terminal unsaturation, it is expected that addition/polymerization is the principal mechanism by which they react in a rubber compound. Addition of co-agent to these polymer formulations suppresses the side reactions and allows crosslinking to occur via tighter network formation (Henning, 2005). These additives are used to improve the physical properties and the processability of peroxide cured elastomers. Properties which are generally enhanced by the use of co-agents are improved heat resistance, better mechanical properties, improved resilience, increased abrasion resistance, improved rubber to metal adhesion (Costin, 2006). Co-agents are normally classified into two broad categories, based on their state and rate of cure (Dikland, 1992, 1993a, 1993b)

Type I coagents: Type I coagents increase both the rate and state of the cure. Most of these contain readily accessible unsaturation without allylic hydrogen. So it mainly undergoes addition reaction rather than hydrogen abstraction. They include multifunctional acrylates and methacrylate esters, bismalamides, etc,. The zinc salt of acrylic and methacrylic acids also belong to this group.

Type II coagent: Type II coagents increase only the state of cure. Coagent of this type contains both readily accessible vinyl unsaturation and abundant number of easily abstractable allylic hydrogens. They include polybutadiene, allylated species like triallyl cyanurate (TAC),Triallyl isocyanurate (TAIC) and diallyl phthalate (DAP) etc,.

Generally in a coagent assisted peroxide cure system, it is well established that the most favorable reaction is crosslinking via coagent molecule (CM). However, several competing reactions like formation of coagent bridges or domains (CD) (homopolymerized coagent compound) may also occur between two effective crosslink points and pendent coagent bridge grafted on the polymer chains. When a coagent domain is grafted to the polymer chain, the effect can be similar to the addition of reinforcing filler with high modulus. The resulting measurable outcome is high crosslink density. A conceptual model of crosslink formation and coagent bridge formation of coagent assisted peroxide system is shown in Figure 1.5.

(i).   Crosslink derived from peroxide only
(ii).   Crosslink derived through coagent domain formation (inefficient use of coagent)
(iii). Crosslink derived through coagent molecule (efficient use)
(iv).   Coagent domain grafted to polymer network (behaves as reinforcing filler grafted to polymer chains)

Figure 1.5: A Conceptual Model of Coagent Assisted Peroxide Cured Polymer Network

The actual state is a combination of the above mentioned various reactions. However, the balance of formation of coagent domains (homopolymerization) over polymer grafting of coagent domains would presumably depend on concentration of coagent, polarity difference between coagent and polymer (solubility parameter) and adequacy of mixing.

1.9 Applications of TPVs

The major application area for TPVs is the automotive sector [White et al., 2009; Legge and Holden, 1987). They found use in hose coverings, air inlet duct covers, gaskets, seals and vibration dampers. Recently co-extruded profiles involved in the weatherseals and interior trim components. The application area is further extended to building construction, house hold articles, electrical cable, food packing, hospital needs and other mechanical goods. Due to its thermoplastic nature, TPVs show the excellent way with the "green movement" for the recycle of polymeric materials. The electrical properties of TPVs are made use in the application such as insulator jacketing materials, wire and cable coverings. The inertness and durability of polyolefinic TPVs have enabled their use in several electronic applications like telephones, electronic appliances, duplicating machines and soft touch household articles. In a nutshell, approximately one-third of TPVs continue to be applied for automotive uses, although development effort is heavily concentrated towards the automotive industry with the aim to penetrate deeper into the weatherseals and gasket markets.

1.10 Scope and background of the work

Literature survey reveals that thermoplastic vulcanizates are the fastest growing polymeric materilals and continuously replacing the thermosetting rubbers in almost all fields of applications. In several application areas, especially automotive sector has chosen to utilize TPVs in place of thermoset rubbers and other TPEs for a number of benefits. Opportunity to reduce cost is paramount. This is resolved as a result of faster production rate, lower part weight by virtue of a lower specific gravity, recyclability and flexibility in design and development of parts to take full advantage of processing and properties capabilities. Among various types of TPVs available in market, most commercial TPVs are based on blends of EPDM (saturated main chain, having excellent stability against heat, oxygen and ozone) and PP (high melting point, high crystallinity, having rigidity and high heat and oil resistance). These PP/EPDM based TPVs are traditionally crosslinked with acid activated resol resin, commonly known as phenolic resin. There are two major problems associated with this particular crosslinking system: (a) hygroscopic of the TPVs i.e., tendency to absorb the moisture even at ambient

temperature and (b) formation of black specks or dark brownish color on storage. These drawbacks of phenolic resins motivate the opportunity to use peroxide as a potential option.

Recently, new family of ethylene-α-olefin copolymers of narrow molecular weight and uniform co-monomer distribution has been produced by using metallocene technology (Dutta, 2008). Commercially available ethylene-α-olefin copolymers were ethylene-1-butene, ethylene-1-hexene and ethylene-1-octene. These materials are generally termed as polyolefin elastomers (POEs) or plastomer. The physical properties of these materials span in the range of plastics as well as rubbers. Interestingly, POEs are compatible with most olefinic material and offer unique performance capacities for compounded products. Due to long chain branching and better compatibility with polyolefins, ethylene octene copolymer (EOC) evolved into a new class of impact modifier for polypropylene, replacing the conventionally used EPDM to produce both TPO and TPE (McNally *et al.,* 2002; Walton, 2004). Furthermore, the availability of EOC in pellet form opens window for continuous compounding to produce the blends. As mentioned previously, simple rubber-plastic blends (PP-EOC blends) do not provide sufficient resistance to compression or tension set particularly at elevated temperature or under prolonged deformation. In order to overcome the above mentioned drawbacks, dynamic vulcanization process is adopted owing to attain desirable improvement in certain properties useful for various specific applications. Therefore, the current focus of the research is to prepare novel TPVs based on PP and EOC.

Besides selecting the type of polymer, crosslinking system employed also plays an important role in determining the final performance properties. Several crosslinking agents are used in the preparation of TPVs such as phenolic resin, peroxide and silane crosslinking system. Phenolic resin gained considerable commercial importance but still the formation of black specks motivates the development of other potential crosslinking system. In this particular PP/EOC blend system; phenolic resin is ineffective, since it needs the presence of double bond to form a crosslinked network structure. Peroxides can crosslink both saturated and unsaturated polymers without any reversion characteristics. The formation of strong C-C bonds provides substantial heat resistance and good

compression set property without any discoloration. It has been well established that PP exhibits β-chain scission reaction (degradation) with the addition of peroxide as shown in Figure 1.6. Hence the use of only peroxide is limited to the preparation of PP based TPVs. An alternative approach to overcome the above mentioned drawback could be the introduction of a compound that not only improves the efficiency of peroxide during crosslinking, but also decreases the extent of degradation. Generally, coagents are multifunctional vinyl monomers, which are highly reactive towards free radicals either by addition reaction and/or by hydrogen abstraction. Some of the benefits that coagents afford are improved heat aging, high tensile and tear strength, high modulus and hardness, increased abrasion resistance, better hot tear properties, improved dynamic properties, excellent adhesion characteristics. Chain-scission also could be minimized by stabilizing the PP macroradicals by addition reaction across the double bond in the vinyl monomer (coagent) (Williams, 2003). Hence addition of coagent in the PP/EOC blend may increase the crosslinking efficiency in the EOC phase and decreases the degradation in the PP phase
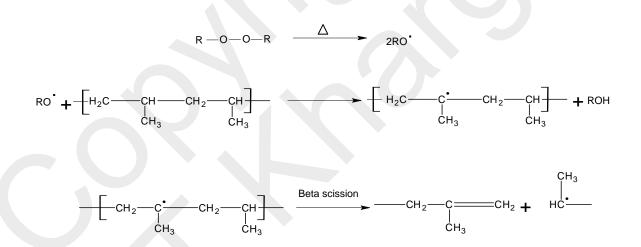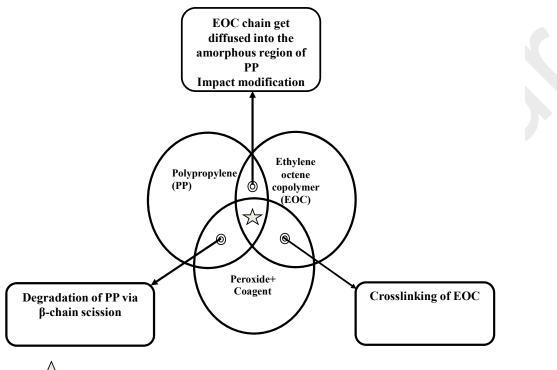

Figure 1.6: Simplified Reaction Scheme for Peroxide Degradation of PP

by β – Scission

General scheme of effect of peroxide in the PP/EOC blend is shown in Figure 1.7. It is important to note that, only limited literature is available on the peroxide cured PP/EOC TPVs. Some research in this field has been done in the industrial area, but little

is openly published because of commercial sensitivity. Lai *et al.* (2005) and Li and kontopoulou (2006) studied the fracture mechanism and nature of deformation on peroxide cured PP/EOC thermoplastic vulcanizates. However, some extensive and systematic study on the development of peroxide cured PP/EOC TPVs is still lacking. Therefore the basic aim of the investigation is to develop peroxide cured PP/EOC TPVs.

Figure 1.7: General Scheme on Effect of Peroxide on the PP/EOC Blend Components

1.11 Objectives

1. To explore the possible use of ethylene octene copolymer (EOC) as a potential alternative to EPDM in the preparation of TPVs

2. To widen the potential use of peroxide in the field of TPVs.

3. To find a proper peroxide/coagent combination and to optimize their concentration with special reference to the final performance properties.

The mechanical, rheological, thermal and morphological properties of the PP/EOC TPVs were evaluated to get deep insight into the micro and macro structural changes that take place during dynamic vulcanization. Furthermore, nature of deformation and mechanism of failure have been also studied in detail.

1.12 Structure of the thesis

The present investigation involves the preparation and characterization of TPVs based on PP and EOC. To achieve the above mentioned objectives, the entire work was explored in seven chapters.

The **first chapter** consists of brief review of the state of art of dynamic vulcanization, earlier work reported including the fundamental knowledge about peroxide/coagent crosslinking system and scope of the present work.

The **second chapter** details the experimental procedure adopted in the present investigation, the details of polymers used, preparation and processing conditions involved, characterization techniques and experiments used.

Chapter three deals with the effect of various peroxides on the preparation of PP/EOC TPVs. Three structurally different peroxides, namely dicumyl peroxide (DCP), tert butyl cumyl peroxide (TBCP) and di-tert butyl peroxy isopropyl benzene (DTBPIB) were taken for investigation. The study was also broadened to understand the influence of molecular characteristics (particularly molecular mass) on the morphological evolution of the blend components and on the property enhancement of the samples prepared by dynamic vulcanization process. Two types of ethylene octene copolymers having the same octene content and molecular mass distribution but differing in their molecular masses were taken. The study was focused at a fixed blend ratio and characterized to understand the structure-property relationship.

Chapter four mainly focused to study the addition of coagent in the peroxide cured PP/EOC TPVs. This chapter was separated into two parts. The first part was to understand the effect of three structurally different coagents namely, triallyl cyanurate (TAC), trimethylol propane triacrylate (TMPTA) and N, N'-m-phenylene dimaleimide

(MPDM) on the dicumyl peroxide cured PP/EOC TPVs. Detailed comparsions of different coagents on the mechanical, morphological, rheological and thermal properties are studied in detail. The second part of the study deals with the investigation of a specific coagent: 1,2-polybutadiene and its effect on the DCP cured PP/EOC TPVs. The special interest in such coagent is deserved from its olefinic, non-polar and structural similarity with the base polymers.

Chapter five deals with the effects of mixing sequence on the peroxide cured PP/EOC TPVs. Three different mixing sequences were employed (a) preblending method- melt mixing of PP and EOC followed by dynamic vulcanization (b) phase mixing method-curative master batch of EOC added in molten PP (c) split addition method- preblending procedure followed by addition of half part of PP (dilution of dynamic vulcanizate). Furthermore, the limits of dynamic mechanical thermal analysis (DMTA) to evaluate the peroxide cured PP/EOC were discussed in detail.

Chapter six depicts a one-to-one comparison of the dynamically vulcanized PP/EOC and PP/EPDM blends using same type of peroxide/coagent combination. The study will cover the deformation characteristics, thermal properties, melt state viscoelastic response and morphology in addition to the recyclability. Scientific discussion behind the nature of microstructure and their influence on the properties are aimed at.

Chapter seven reports the summary and conclusions of the thesis.