CHAPTER 1

INTRODUCTION

In recent years, polymer blends are gaining technological importance due to their compromise set of properties. They offer advantages in processing and can be economically more viable than the single polymers. A particular polymer may have a set of mechanical properties superior to the other polymers, while the others may be rich in a different set of properties which are lacking in the former. By blending of polymers several properties can be improved, sometimes without sacrificing the others. For this it is necessary to know which polymers can be successfully blended and what underlying factors influence the results.

Processability and mechanical properties of rubber blends depend mainly on their compatibility and miscibility. Miscible rubber blends are those which are homogeneous throughout in microscopic scale. Compatible rubber blends are miscible only in a technological sense i.e. they can be co-vulcanized after blending and the properties are improved. Bulk morphology is another important consideration which determines the physical properties of rubber blends. The process of blending, the phase viscosity and other processing conditions influence the morphology of a blend. In most cases either of the two components (in the case of a diblend) forms a continuous phase in the matrix with the other phase dispersed in it. Generally the component with lower viscosity forms the continuous phase.

1.1 BLENDING & CHARACTERIZATION OF RUBBER BLENDS

There are several processes of blending which include latex blending[1,2], solution blending[3,4] solution and latex blending[5,6], conventional mechanical[7,8] and mechanochemical[9,10] mixing method, and powdered blending in special cases. These blends are characterized by physical and chemical techniques like microscopy[3,11-14], solubility[15], optical method[16,17], thermal and thermomechanical analysis[18,19], dielectric relaxation[20], infrared spectroscopy[21], NMR spectroscopy[22], X-ray analysis[23,24], gas chromatography[25] and other miscellaneous techniques[26]. Corish et al.[27] and McDonel et al.[28] have reviewed recently rubber-rubber blends. The influence of structure on compatibility has been discussed by Marsh et al.[12]. Only a few miscible rubber-rubber blends have been reported[4,29-31]

1.2 APPLICATIONS OF RUBBER BLENDS

Rubber-rubber blends are widely used for the manufacture of both small and large rubber articles. Examples include tire, belt, cable etc. Tire industry is consuming almost more than half of the total consumption of rubber. It is interesting to note that the major components of tire except tread ply have been successfully compounded using rubber blends. In cable industry the cover rubber is made mostly from elastomer-elastomer or elastomer-thermoplastic blends for better resistance to abrasion,weathering, heat, chemicals etc. Conveyor belt is another rubber industry using elastomer blends. For top cover ethylene-propylene-diene rubber (EPDM) is blended with natural rubber, chloroprene rubber (CR), chlorobutyl rubber (CIIR), bromobutyl rubber (BIIR) etc. By this way the slow cure characteristics and low tack property of EPDM rubber are improved giving rise to better physical and mechanical properties.

1.3 SOME USEFUL RUBBER BLENDS

The abrasion resistance and elasticity of natural rubber (NR) has been improved by blending with polybutadiene rubber (BR), finding application in tire tread[32]. The processing characteristics of car and truck tire tread recipe based on blends of BR and styrene-butadiene rubber (SBR) or NR have also been reported[33]. Some authors claimed that this blend gives very good tire performance at lowest cost[34,35]. More milage(i.e., increased miles of service per compound cost) has been obtained by blending BR-black master-batch with SBR-black masterbatch instead of blending the elastomers themselves[36].

Improved resistance to cutting by blending BR with SBR, NR and synthetic isoprene rubber has been reported elsewhere[37]. The blend of NR and Buna - S (styrene-butadiene copolymer)[38] gives good resistance to flex cracking, processing and vulcanizing. Fujimoto et al.[39] reported that mixtures of SBR, NR and a low molecular weight substance yield better fatigue property. Good mechanical properties are achieved by blending two synthetic polyisoprenes (Cariflex IR 305 and IR 500) with NR[40]. Optimum technical properties of carcass vulcanizates have been obtained by mixing stereoregular cis-IR and α -methylstyrene polybutadiene rubbers at a ratio of 1:1 as reported by Levitin et al.[41]. The blending of ethylene-propylene-diene rubber (EPDM) with butyl rubber gives enhanced heat resistance property[42,43]. The blends of EPDM with liquid diene rubbers decrease the scorch rate whereas it is enhanced by blending EPDM with chloroprene rubber[44]. Blends of EPDM and chloroprene rubber are used in tire sidewall[45-47]. In some cases EPDM and EPM are blended with highly unsaturated diene rubbers for ozone shielding property[48-50]. Resistance to chemicals and reduction in compression set are the other advantages[51]. Satake et al.[52] reported that EPDM can be blended with SBR and SBR/BR blend for use in tire tread; no antioxidant is needed. Moderate resistance to oil and ozone and an acceptable level of general mechanical properties can be obtained by blending EPDM with nitrile rubber (NBR)[53].

Butyl rubber is blended with NR for use as the inner liner of tubeless tires for its good resistance to mechanical damping[54] and permeability[55]. Mekel and Bierman[56] reported that a triblend based on IR/NR/BR compounds provides advantageous properties suitable for giant tire treads.

1.4 PROPERTIES OF ELASTOMER BLENDS

1.4.1 Processability

Blending of polymers by mechanical means is of more importance compared to other blending methods[7] as this produces, in a short time, macroscopically homogeneous blend which is desired for better vulcanizate properties. This can be carried out either in a two-roll mill, internal mixer or mixtruder. For better dispersion of ingredients during mixing on an open mill the viscosities of the component phases should be of comparable magnitudes[57]. For blending elastomers having different cure rates, it is better to prepare masterbatches of elastomers and curative[57,58] and then blending them in required proportions. This method has been found very effective[4,42,59] in mechanical blending technology. Evans[60], however, has found that for the blend of nitrile and chlorobutyl rubbers, mixing of the curatives in a preblend of the elastomers gives better properties. Comparison of mill mixing and banbury mixing is described in various literatures. Sundo[59] has reported that for NR-SBR blend mill mixing gives more homogeneous blend than Banbury. Hess[11] has observed distribution of polymer components and proved that mixing in Banbury is less critical as reported by others[57]. McDonel et al.[28] has also discussed the influence of mixing conditions on the distribution of compounding ingredients. The milling behaviour of different rubbers has been reported by many workers[61-65] paying due consideration to material viscosity, nip distance, roll temperature and adhesion characteristics of the elastomers with the roll surface. Some mathematical relations have also been deduced.

1.4.2 Rheology

One of the several reasons for blending of polymers is to get better processability. The improvement may be seen in the lowering of the stock viscosity or getting a material having a smooth flow property. One may expect that the die swell behaviour and shrinkage will be low and that the processing behaviour of the blends may be the intermediate with respect to that of the pure components. It is well known that blending of polymers of different types produces heterogeneous systems. Difference in molecular structure and molecular interaction results in blends having anomalous rheological behaviour. It has been reported[66] that flow of polymer blends should be regarded as the combined flow of materials of differing viscosity. From earlier studies[67,68], it has been concluded that blends of polymers of identical chemical structures show viscosities similar to or greater than the additive values of the individual components. Theories are available[69-71] to predict the viscosity of the blends.

Rheology of elastomers and their blends has been studied by many authors[72-78]. According to Everage[79] an elastomer can rearrange its molecular structure during its flow through a pipe to follow the minimum energy dissipation principle. Lee[80] and Lee et al.[81] have studied flow property to find out the distribution of carbon black in a blend of elastomers and its influence on the blend vulcanizates. They have reported that the viscosity of SBR-BR blend is independent of carbon black distribution, whereas the elastic properties were found to vary. According to Van Oene[82], the internal circulation occurring in the dispersed particles of a sheared blend may also contribute to the reduction in viscosity. Turner et al.[83,84] pointed out that wall slippage occurs during the passage of EPDM rubber through capillary under high rate of shear, thus resulting in a reduction of shear viscosity. A similar observation was recorded by Shih[85] when working with a blend of fluoroelastomer and a small fraction of EPDM rubber. Lipatov et al.[86] have generalized the phenomenon for various blend systems. Cotton[87-90] has investigated in details the influence of carbon black and other ingredients on processability (mainly extrusion) of different elastomers and their blends. The addition of a third component (say carbon black) in an elastomer blend influences its shear viscosity and die swell. Sircar et al.[91] have pointed out that in a blend, a reduction of die swell is achieved by the addition of carbon black in that phase whose die swell was found to be most reduced by the presence of filler. Some authors[92] observed that the distribution of vulcanizing system has also some influence on the die swell of elastomer blends. Thus in a blend of C-black filled SBR and isoprene rubber, the diameters of the extrudates obtained with the thiouram were generally higher than those obtained by using N-cyclohexyl-2-benzothiazyl sulphonamide/sulfur system. The dependence of extrudate die swell on temperature has been investigated by Beynon and Glyde[93], who reported that the die swell is inversely proportional to the temperature of extrusion.

1.4.3 Tack and Green Strength

For building operation of a complicated rubber article (say tire or any plied up product) tack and green strength are two most important criteria. The individual parts of the article are assembled first in the preforming stage, before the green article proceeds for vulcanization. An optimum level of tack is needed for this processing operation. Too much tack will lead to air entrapment and trouble in repositioning. If there is little tack the individual components of the green article cannont be held together, thus leading to low productivity and increased scrap. Green strength is needed so that the uncured article will not creep before moulding, or tear due to expansion that occurs during moulding.

For a compound to exhibit high tack, three conditions are essential:

(i) intimate molecular contact of the adhering surfaces,
(ii) interdiffusion of molecular segments across the interface, and
(iii) capability to resist the rupture of the entanglements formed i.e. good green strength.

The tack property of an elastomer can be improved by the addition of a tackifier e.g. a resin. But this may affect the other technical properties. By blending two or more elastomers the tack can be improved without sacrificing the other technical properties. In fact many synthetic elastomers (e.g. SBR, BR, EPDM, NBR), defficient in tack property, are being used mostly in combination with NR for enhancing tack. Improvement of tack in the synthetic rubbers will depend upon the method of blending as well as the flow behaviour of the constituent elastomers.

Several authors have worked on tack and green strength of single elastomers and elastomer blends. Morrissey[94] has reported that in a series of blends of NR with other synthetic rubbers, the level of tack paralleled the NR content. Hamed[95-97] has observed that the tack and green strength of NR, SBR and NR-SBR blends are dependent on the flow criterion of the elastomers. NR, being strain crystallizing, exhibits a good level of green strength even at higher molecular breakdown and hence exhibit tack strength higher than SBR. The green strength of SBR can be raised by increasing the molecular weight, but at high molecular weight region SBR is devoid of tack. These authors have also pointed out that tack is contact limited. Others confirmed that intimate molecular contact[98-100] and interdiffusion[101-105] are of paramount importance in obtaining good tack of a rubber stock. Some authors[106,107] have reported that in unvulcanized soft elastomers the scale of contact zone is also of considerable importance. Chain cavities in a polymer chain, consisting of intra-chain free space and inter-chain free space play a prominent role[108,109].

NR having larger size cavities than SBR, shows higher tack than SBR. EPDM has only very few cavities in its propylene segment and shows very poor tack. Hamed[110] observed that crystallinity and semicrystallinity in materials severely limit the chain mobility which is most essential for tack bond formation. For this reason ethylene-propylene copolymer (EPM) and EPDM rubber exhibit poor tack. Recently Bhowmick et al.[111] have discussed the adhesive tack of EPDM rubber. Some authors[112-114] have correlated the high raw tensile strength of NR with its strain induced crystallization to explain its high tack. Some mathematical relations between tack strength and contact time are also available[115]. Gardiner[116] and Corish[117] have found that an interpenetrating morphology of the blends of two elastomers exhibits high tack due to good entanglement. According to Roland et al.[118], in a blend of two components if the component with high autohesive tack forms the continuous phase, the tack strength becomes high. Incorporation of filler in elastomer has a marked influence on tack strength. Bussemaker et al.[119] and Beckwith et al.[120] have reported that the addition of a reinforcing filler to NR increase the tack strength. Bussemaker[121] has also suggested that bound rubber formation is responsible for this increase of tack in filled NR. Beatty[122], however, has explained the phenomenon with the help of increase of green strength of NR due to addition of carbon black.

Addition of carbon-black in SBR decreases tack[123], due to restriction of chain mobility as explained by Hamed[110]. The type of black, however, doesnot have any marked influence on tack[124]. More recently, Roland and Böhm[125] observed that the controlling variable in tack measurement is the ability of the plied surfaces to fuse together. According to Skewis[112], however, tack strength can have a maximum value equal to green strength of a rubber stock. Except NR, a few other synthetic rubbers may also be blended to improve tack[126,127]. With increase in temperature the green strength falls[127].

1.4.4 Technical Properties

The technical reasons for blending of two or more elastomers fall into two broad headings viz., easier processing and better vulcanizate properties. The elastomers with narrow molecular weight distribution (MWD) create difficulty in processing (mixing, extruding and calendering). This may be overcome by addition of processing aids like oil, liquid polymer of low molecular weight etc. But an easier way to achieve it is to blend it with another elastomer having broad MWD like NR or emulsion SBR. The most important factor governing the vulcanizate properties is the distribution of compounding ingredients, mainly filler. Mode of addition of curatives and fixation of curatives in one of the phases have also some prominent effect.

Corish and Powell[27] published a good review on rubber blends in 1974. In a more recent review Roland[128] has discussed the effect of distribution of compounding ingredients on the ultimate properties of rubber blends. Generally blending of elastomers leads to a heterogeneous system in which both the polymer phases are present[129]. The extent of heterogeneity increases after the addition of the compounding ingredients if the elastomers have unequal affinity for these ingredients[4]. This unequal affinity leads to a heterogeneous distribution of filler[27,91,130-132] creating problems especially in the case of tire industry[27]. Many authors[91,132,133] have shown that the properties of a blend can be improved by preferential addition of the carbon black in the blend. Methods of assessing the reinforcing ability of the fillers have also been discussed[134-136].

According to Von Amerogen[114] and Gardiner[137,138] the solubility of sulfur is more in a highly unsaturated elastomer. Therefore, in a blend consisting of NR and a low unsaturated elastomer like EPDM the common vulcanizing agents prefer to migrate from EPDM to NR, thus leading to poor covulcanization (over and undercure take place)[39,20,116] giving inferior vulcanizate properties. According to Leblanc[139,140] the curatives locate initially in the continuous phase. Generally the elastomer with lower viscosity forms the continuous phase.

Compatibility of a low unsaturation elastomer with a high unsaturation one can be improved by controlled interphase crosslinking of the blends. Compatibility of EPDM with high diene elastomers has been improved by this technique[141]. It has been found that better compatibility is possible if the component elastomers have virtually identical cure rate[22]. Ishitobi et al.[142] and Kerrutt et al.[143] have suggested that during co-curing of a blend of EPDM and chloroprene rubber the individual components consume different amount of curatives. Corish and Palmer[10] used radiochemical methods to estimate the distribution of sulfur in black loaded rubber blends. Some authors[144,145] suggested that the use of a long-chain hydrocarbon dithiocarbamate accelerator is beneficial in sulfur cure of EPDM with highly unsaturated hydrocarbons. Hashimoto et al.[146] have discussed that polysuphidic linkages are most effective for interfacial bonding, but Zapp[147] has found that in CIIR-BR blend, the interfacial bonding is correlated with a high degree of monosulphidic linkages. Sometimes the interfacial crosslinking is facilitated by the presence of very small amount of a third component soluble in both phases[148]. Recently, Baranwal and Son[149] have shown that by grafting accelerators into EPDM the co-curing ability of a blend of EPDM and a highly unsaturated diene can be improved, thus leading to good vulcanizate properties. A few workers[129,150] have investigated the dynamic mechanical properties of blends having compatibility (e.g. SBR/BR and NR/BR). It has been reported that interphase crosslinking causes a merging of the dynamic mechanical loss peaks characteristics of the individual polymers.

Apart from the migration of curing system and filler, the migration of other ingredients has also been reported. Thus Corman et al.[151] demonstrated that migration of oil on the elastomer surface takes place depending on the structure of both elastomer and oil. In another study Lewis et al.[152] have shown that migration of antiozonant takes place preferentially from EPDM to SBR during cure.

The cut growth behaviour of a rubber compound is very important. Once a cut has been initiated on the rubber compound its nature of propagation plays a significant role in deciding the service life of the product, particularly under repeated stressing (the fatigue failure). A very good review on fatigue failure of rubbers has been published by Beatty[153]. Gent et al.[154] and Lindley et al.[155] have treated the fatigue failure quantitatively. Gent et al.[154] found that the cut growth per cycle of NR is approximately proportional to the square of the maximum tearing energy attained during cycle. Lake and Lindley[156,157] have studied the role of ozone in dynamic cut growth of several rubber compounds. Thomas[158] has also reported the cut growth behaviour of elastomers under dynamic condition.

Abrasion is another important factor leading to the failure of a number of rubber products. It has perhaps been least understood among the various failures of rubber. Schallamach[159-161] was the first to study the abrasion pattern on abraded rubber surfaces. He has shown that the type of abrasion occurring during high rate of extension is due to tensile failure of the compound. Some workers[162-164] have discussed the importance of viscoelastic behaviour during abrasion. Aharoni[165] pointed out that wear by roll formation is common when bulk deformation exists in the polymer. Some authors[166] claimed that material transfer takes place from one surface to the other during frictional wear. Formation of the free radicals on the rubbing surface has also been reported by these authors. According to Briscoe[167,168] the mechanism of particle separation during wear in polymers may vary broadly. Grosch et al.[169] have studied the influence of hysteresis on rubber wear. Southern et al.[170] have applied the fracture mechanics to understand the mechanism of wear and reported that the growth of crack plays an important role in the abrasion process.

1.5 SCANNING ELECTRON MICROSCOPY (SEM) STUDIES ON FRACTURE SURFACES OF RUBBER

Application of SEM in polymer research is quite recent in origin. It is used to understand the mechanism of failure of rubber vulcanizates by studying the fracture surface of the sample and the reinforcement characteristics of filler used as compounding ingredients. SEM was used by O'Conner[171] to observe the fracture surface of short-fibre reinforced rubber composite with a view to find out the degree of alignment, the uniformity of fibre dispersion and the extent of fibre-rubber adhesion. Bascom[172] investigated fracture mechanism of rubber by using the SEM technique. The fracture surface of a series of gum and filled rubber vulcanizates under different modes of failure has been studied by Bhowmick et al.[173-175]. Murty et al.[176,177] and Chakraborty et al.[178] have used the SEM technique to study the fracture surface of short fibre-rubber composites showing the fibre pull-out failure resulting from poor fibre-rubber adhesion, the role of silica in promoting adhesion, the alignment of fibres in the matrix and the nature of the fracture surfaces obtained in different types of failure tests. Akhtar et al.[179] have predicted the extrusion characteristics of natural rubber/polyethylene blend by observing the extrudate surface morphology through SEM technique. Mathew et al.[180-182] have reported the fracture mechanism at different modes of fracture and the effect of thermo-oxidative ageing of fracture surfaces of NR vulcanizate. The fracture surface of unfilled NR vulcanizates shows a rough zone followed by a comparatively smooth region. The presence of antioxidant or the change in vulcanizing system does not show any change in the mode of fracture as shown by their SEM studies. Deuri et al.[183,184] have studied the fracture surfaces of unaged and aged EPDM vulcanizates at different modes of failure. They have correlated the tensile strength with the distance between crack lines and tear lines. Effects of flaw size on tensile rupture have also been reported. In general, EPDM surface gives a smooth feature. After ageing, the roughness of the fracture surface for NR vulcanizate reduces. For carbon black filled vulcanizates, the whole surface appears rough with large number of curved tear lines indicating a strong polymer-filler interaction.

1.6 SCOPE OF THE PRESENT WORK

The use of blends of elastomers in place of single elastomer is increasing day-by-day due to several technical reasons. It is evident from the foregoing discussion that the choice of elastomers depends on several factors. They must be cure compatible and allow covulcanization. After blending their processing characteristics should be very good and product performance better over the component elastomers. All these properties must be understood fully to exploit various rubber blends. Tire represents the maximum use of rubber-rubber blends. The other major applications include cables and conveyor belt, specially for high temperature application. The present investigation deals with the detailed study of blends based on ethylene-propylene-diene rubber (EPDM) and bromobutyl rubber (BIIR). These blends may find application in the manufacture of conveyor belt for high temperature service. The features that make EPDM rubber for this application include its excellent resistance to heat and oxygen, high resistance to permanent deformation, very good resistance to flex cracking and impact, excellent abrasion resistance and outstanding resistance to ozone and weathering. The bromobutyl rubber is used for its following properties : high ozone and weather resistance, much faster cure rates with reduced curative levels, very good resistance to heat and very good cure compatibility, cured adhesion to other elastomers and improved air impermeability. The salient advantages of blending BIIR with EPDM are to improve tack and adhesion, impermeability and damping characteristics of EPDM. Although a lot of work has been done on elastomer blends, studies on the blends of EPDM and BIIR rubbers are lacking. In this investigation emphasis has been given to get a thorough idea of all the characteristics of EPDM and BIIR rubber blends starting from raw material to the finished product (conveyor belt).

The mechanical and physical properties of an elastomer blend depend to a great extent on the process of blending. The most convenient way for blending solid (dry) elastomers is mechanical mixing. Mostly an internal mixer is employed for this. A two-roll mill is necessary for sheeting operation of the rubber mix obtained from an internal mixer. For ease of addition of ingredients and safety operation the compound is desired to be banded on the slow roll (front roll). But in some cases the compound has a tendency to go to the fast roll (back roll). Also other problems like roll sticking, bagging etc. arise, thus hampering smooth processing. In this investigation milling behaviour for blends of EPDM and bromobutyl rubber has been reported using different friction ratios and at different temperatures. These data have been compared with those of more common NR/BR blends.

Rheological behaviour (flow properties) of the component elastomers are very important for processing, moulding and product designing from an elastomer blend. In the present thesis, rheological investigations along with the die swell studies for pure EPDM, pure BIIR and their blends have been carried out in details.

For preforming operation of a complex rubber article (say tire or conveyor belt), tack and green strength are the two most important criteria. The compound must possess an optimum tack to hold the components in position until and unless the moulding is over. Green strength is needed to prevent any deformation during handling of the green article. These two properties have been studied thoroughly at different blend ratios and temperatures (both contact & testing) for both unfilled and filled blends of EPDM and BIIR. The effect of mode of incorporation of fillers (china clay & carbon black) has also been examined.

Blending of elastomers is done mainly to get improved technical properties of the end products. Distribution of compounding ingredients has a major effect on the properties, specially for the elastomers of different natures. The elastomers in this investigation have different polarity. Therefore, it is expected that the distribution of compounding ingredients will be different. The technical properties of blends of EPDM and bromobutyl rubbers have been studied in this thesis at different blend compositions and modes of addition of ingredients. Properties of aged samples have also been measured. Further studies have been conducted to understand the adhesion behaviour between the blend components by partially prevulcanizing the compounds and mixing them.

During service the rubber articles pass through some severe conditions which may damage the belt. For a coveyor belt compound crack propagation under repeated stressing and abrasion of the cover rubber are two very important properties which need to be taken care of. In the present investigations these two properties have been studied in quite details at different blend compositions and at different temperatures. Microscopic examination of the failure surfaces has been done to understand the mechanism of failure.

At the end of the study, the blend of EPDM and BIIR has been used to manufacture and testing of a specimen conveyor belt. Retention of physical properties including adhesion after prolonged ageing has been investigated in order to determine the grade of the test belt.