Chapter-1

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1.0. Versatility of polymers:

Polymeric materials have already become very important in the field of modern material science, industry and in our daily life. Some of its salient features, which remain unchallenged till date, by any other conventional materials, have enabled it to occupy such a unique position. The versatility of polymers in respect of its performance in diverse applications has made it the most important choice to cater to the ever increasing demand of needs in our modern daily life. It is because of its durability, inertness to weather change, easy and inexpensive process of fabrication, low weight to volume ratio, reasonably low price, scope of having a wide range of properties by incorporating suitable additives and last but not the least its recyclability.

1.1. Polymer blends:
1.1.1. General overview:

The technology of blending polymers – thereby reducing the weakness of one by the strength of the other revolutionized the world of material science through the development of a host of new polymeric materials without any invention of new monomer/new chemistry. The ability to combine the existing polymers with proven characteristics to achieve desired set of commercializable properties not made by any of them singly, offers the advantage of new scope of research and development at marginal expenses compared to the cost of development of new monomers and polymers to yield a similar property profile. An additional advantage is the much lower capital expenses involved with scale – up and commercialization. Another specific advantage of polymer blends over new monomer/polymer compositions is that the blends can often offer property profile combination not easily obtainable with new polymeric structures. In the rapidly emerging technology landscape, polymer blend technology can quickly respond to the developing needs, much faster than the time consuming R & D involved with new monomer/polymer development. The technical response to emerging needs is now first directed at polymer blend technology to determine if such needs can be met by any blend instead of developing wholly new polymeric
compositions. The role of polymer blend technology is pervasive in the products of our everyday life.

**Some important definitions related to polymer blends [1]:**

**Miscibility:** Miscibility is considered to be the level (scale) of mixing of polymeric constituents of a blend yielding a material which exhibits the properties expected of a single phase material, which can only be ascribed to molecular level of mixing. Microstructure can be expected in the 1 – 2 nm range. Miscibility is established from thermodynamic relationships.

**Immiscibility:** A blend is considered immiscible if it is separated into phases comprising primarily of the individual constituents. Phase separation is also established from thermodynamic relationships.

**Partial Miscibility:** A blend is considered partially miscible if there exists phase separation but each polymer rich phase contains a sufficient amount of the other polymer to alter the properties of that phase (e.g., the glass transition temperature).

**Compatibility:** Compatibility is a general term used to imply useful properties of a polymer blend even though phase separated. Generally, the mechanical properties are employed as a reference to the degree of compatibility. Compatibilization of incompatible polymer blends is a major area of research and development. The degree of compatibility is generally related to the level of adhesion between the phases and the ability to transmit stress across the interface.

**Microheterogeneous:** A blend is described as micro heterogeneous if it consists of a wide range of compositionally different phases. While the blend may exhibit a single glass temperature peak, it is comprised of a distribution of glass transition between the component values.

### 1.1.2. Technological overview of alloys and blends:

The understanding of the potential of polymer blend technology to design specific compositions to meet application requirements is of primary importance. Individual polymers have a singular property profile capable of meeting only a limited number of applications. The application potential of any polymer can be greatly enhanced by employing the principles of blend technology.
In order to mix two components and obtain a product, which doesn’t undergo complete phase separation during processing or end use, a minimum thermodynamic compatibility is necessary. Beyond this level of compatibility, greater attractive forces between the constituents serve to enhance the properties of the final product.

In general for two component mixture, any property can be described by the following empirical equation [2]:

$$P = P_1 C_1 + P_2 C_2 + I P_1 P_2$$

where, $P_1$ & $C_1$ are the component property and concentration terms and $I$ the interaction coefficient.

For $I > 0$, the resultant polymer has better properties than the arithmetic average of the property of the individual component.

For $I = 0$, the properties are just additive.

For $I < 0$, the resultant polymer has properties, worse than the arithmetic average of the components.

Alloys are synergistic polymer combinations ($I > 0$), if the components are thermodynamically compatible, or strong intermolecular forces make the mixture behave as a single phase material with one single transition ($t_g$) e.g., PS modified PEO (Noryl) or PS modified PPE (Prevex). For these blends, PS reduces the melt viscosity sufficiently to allow easy processing and largely retaining strength (modulus), impact resistance, hydrolytic stability of the PEO or PPE.

Blends show less intense thermodynamic compatibility and therefore exhibit discrete polymer phases with multiple glass transitions. In general, the properties of blends reflect the weighted arithmetic average of the properties of the constituents ($I = 0$) e.g., PC/ABS blends. Specific gravity, coefficient of thermal expansion, flexural modulus etc. are arithmetic averages [2].

1.1.2.1. Preparation of blend/alloy:

There are different ways to mix polymers: melt blending, solution blending, latex or dispersion blending.

In melt blending an extruder is predominately used to prepare blends. Compatibilizing agents may be incorporated at the same time in order to enhance
the synergism to prevent phase separation and to enhance the physical and mechanical properties; for example: block co-polymers, the co-monomers being the precursor of the individual homopolymers to be blended in question.

1.1.2.2. Selection of polymer combinations:

Polymer components, which make the blend, are generally selected to complement each other in one or more of the following properties: costs, processability, mechanical properties, warpage, chemical resistance, thermal performance etc.

Blends are typically viewed as cost savings: the more expensive polymer is combined with the less expensive product to provide adequate performance at a significant reduced price (ABS/PC, ABS/Polysulfone, PES/PEEK etc.). In addition, the development of a synergistic property profile (I > 0) is also another mission.

Very often crystalline and amorphous polymers are blended to achieve a specific property range. Crystalline polymers have excellent chemical resistance, good mechanical properties (especially with reinforcements), low viscosity while molten whereas amorphous polymers provide good dimensional stability (no warpage) and excellent impact strength. Within the range of thermodynamic compatibility a harmonic balance of properties of different polymers is sought about.

1.1.2.3. Phase behavior:

A prime consideration in any polymer mixture is the degree of homogeneity of the blend. Immiscible blends form multiple phases for all ratios of composition, the composition of each phase being essentially those of the individual component. Miscible materials mix completely at all blend ratios forming a single phase. Partially miscible systems are very frequent. These blends are miscible at a selective composition and phase separation occurs at other compositions.

The thermodynamics driving force for mixing is minimization of the free energy of the system \( \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \) [2]. Thus if the free energy is
positive, the system will be immiscible. If the free energy of mixing is negative at any composition, some degree of dissolution will occur and the system will be at least partially miscible. For the system to be miscible, the second partial derivative of composition of the free energy must be positive. Blends, which are miscible at one set of conditions may undergo phase separation if conditions are changed. As such, variations in temperature, pressure and/or shear stress can induce phase separation.

The kinetics of the phase separation and the morphology of the resulting blend depend upon the stability of the homogeneous mixture at the given condition. The relative contribution of the combinatorial entropy of mixing for polymers, due to the much larger size of the molecules, is small, thus the driving force for mixing is only the enthalpy $\Delta H_{\text{mix}}$. As such, even relatively weak repulsion forces (non-polar molecules) ($\Delta H_{\text{mix}} > 0$) are sufficient to oppose mixing. The glass transition of polymer blends is strongly affected by the degree of phase separation at segment level. The determination of the glass transition temperature(s) of a blend is a straightforward method to assess the degree of mixing of a blend. Generally, the presence of a single, composition-dependent $T_g$ at a temperature between the glass transition temperatures of the component polymers is accepted as evidence of miscibility. Conversely, two-phase blends exhibit two glass transition temperatures. If the polymers are completely immiscible, the glass transition temperatures of the blend will equal the glass transition temperatures of the component polymers. If there is partial miscibility, however, the exact positions of the glass transition temperatures in a two-phase blend will depend upon the relative amount of each component in each phase.

### 1.1.2.4. Morphology and compatibilization:

Miscibility refers to mixing in the amorphous phase and doesn’t preclude crystallization of the blend components. In the absence of crystallinity, miscible blends consist of a single amorphous phase. Because of the lack of structure, miscible amorphous blends are transparent. Transparency therefore is often used as evidence of miscibility. However this is not a proof, as immiscible blends can
also be transparent if the dispersed phase refractive indices match that of the matrix.

Immiscible and partially miscible blends are more common, than miscible blends. The properties of these blends are highly dependent upon its phase behavior and morphology. When separate phase are present and the proper morphology is obtained, it is possible to combine the desirable attributes of each polymer into a single material. Phase separated blends, thus offer the potential to retain the desirable properties of both components. However the properties related to ductility and toughness, are often less attractive in the blend than in either of the components. This is due to a large extent to the extreme dependence of these properties on the morphology. Toughness requires a homogeneously dispersed phase of spherical particles. High interfacial tension opposes particle breakdown, during melt mixing for example, and causes coalescence. Consequently, the dispersion of the component in many immiscible blends is very poor. Large interfacial energies produce sharp phase boundaries, which results in poor adhesion between phases. This reduces stress transfer between phases.

In order to overcome these problems, compatibilization technique is used to increase adhesion between phases and to control (stabilize) the dispersion of the dispersed phase. The goal of most compatibilization schemes is to increase the properties of the blends while retaining the two-phase nature and not to promote miscibility of the blend.

1.1.3. Classification of polymer blends:

Polymer blends can be classified according to the miscibility of the participating constituents, use, overall composition, morphology, physical nature and type of polymers etc. Some of the major classes of polymer blends are mentioned below:

1.1.3.1. Classification based on chemical composition:

Homologous polymer blends:

These are referred to as the subclass of polymer blends limited to mixtures of chemically identical polymers differing in molecular mass. In such blends, the
two polymers are completely miscible down to the segmental level and exhibit single phase behavior. The properties of such blends are generally proportional to the ratio of the two polymers in them.

**Heterogeneous polymer blends:**

These involve two polymers which are chemically dissimilar and may or may not form a homogeneous single phase upon mixing. The properties of such blends are dependent upon the properties of the components, composition ratio and chemical nature. Blends of polyphenylene ether with polystyrene belong to such category.

### 1.1.3.2. Classification based on miscibility:

**Miscible polymer blends:**

These encompass those polymeric blends which exhibit a single phase behavior. In such cases, $\Delta G_{\text{mix}} \leq 0$, with the molecules of one component intermingling with the other to overcome partially the intermolecular cohesive forces between the individual polymers. PVC - $\alpha$ methyl styrene - acrylonitrile copolymer is an example of such type [3].

**Immiscible polymer blends:**

A sub-class of polymer blends that exhibits two or more phases at all compositions and temperature constitute the immiscible polymer blends. A mixture of polystyrene (PS) and polymethylmethacrylate (PMMA) is a typical example of the immiscible system [4].

**Partially miscible polymer blends:**

These blends constitute those blends that display a ‘window’ of miscibility i.e., they are miscible only at certain concentrations and temperatures. A clear one phase mixture is obtained when PS is mixed with poly (vinyl methyl ether) and fluxed on a mill at 80°C which however exhibits two phases when the temperature is raised to 140°C. The process is reversible [5].
1.1.3.3. Classification based on compatibility:

Compatible polymer blends:
These comprise a sub-class of polymer blends which are homogeneous to the naked eye. These are superior in mechanical properties than the incompatible blends and are useful as commercial products. Compatibility is a relative term in the sense that the phase size of the blend will change with time depending on the kinetics of phase separation.

Blends of bisphenol A polycarbonate (PC)/acrylonitrile-butadiene-styrene (ABS) have been widely used as commercial products for many years [6].

Incompatible polymer blends:
Blends heterogeneous to the naked eye comprise such type. Styrene-butadiene-rubber (SBR)-polystyrene (PS) blends are relatively incompatible even though they are both non polar polymers and their solubility parameters differ by only 1.0.

1.1.3.4. Classification based on mixing methods:

Mechanical blends:
This involves mechanical blending, where two polymers are blended with high energy intensive machines, e.g., extruders or open rolls, a type of mechanochemical mixing, in which the shear action generates free radicals through polymer degradation reactions.

The free radical thus induced by mechanochemical action subsequently reacts with other structurally different polymer present to form true chemical grafts between the two components which can result in single phase structure. Most of the polyolefin blends e.g., blow moulding grade polypropylene (PP)/linear low density polyethylene (LDPE) are produced by mixing on an extruder. Various rubber blends are prepared by mill mixing [7].

Solvent cast blends:
The polymeric components are brought into solution by adding a suitable diluent that lowers the temperature and shear force necessary for satisfactory
mixing. The removal of the diluent may often cause environmental pollution and changes in phase morphology of the blends and in severe cases, it may cause complete phase separation because of the differences in solvent power of the two polymers.

Natural rubber (NR)-Styrene butadiene rubber (SBR) and butyl rubber (BR)-NR blends were mixed in a 5 \% solution of benzene and the solvent was evaporated [8]. They found the dispersed domains appearing much larger than the same obtained with mechanical mixing.

**Latex blends:**

These blends are prepared by mixing polymer lattices followed by coagulation. It has been reported that a BR latex blend with NR or SBR gives an improved dispersion of carbon black [9].

**Blends prepared by reactive processing:**

The process involves diverse technology, ranging from in-situ polymerization of one monomer to co-reaction of two polymers. It is fast, irreversible, low exotherm and very economical [10], particularly when carried out in a twin screw extruder. This process is specially important in cases in which graft and block copolymers are formed in-situ during the mixing process, which act as effective compatibilizers. An example of this category includes the addition of maleic anhydride modified PP in PP/nylon blends to achieve in-situ formation of graft copolymers of PP and nylon [11]. Such blends may also be produced due to natural reactivity of the polymer groups (e.g., in transesterification of polyethylene terephthalate (PET)/polybutylene terephthalate (PBT) with PC. Curing of one polymer with another reactive polymer as the blend component to form multi component polymeric networks might also be another reactive blending process (self curing of polychloroprene rubber and polyacrylic acid).

Again, blending of polyolefins in presence of peroxide initiator is also a kind of reactive processing. Formation of interpenetrating polymer networks (IPNs) [12], reactive polymeric fillers [13] and dynamic vulcanization techniques [14, 15] are also included in this category.
1.1.4. Factors affecting miscibility and immiscibility:

A number of specific features may contribute to the miscibility and immiscibility of polymer blends [16]. These may be listed in order of commercial importance:

**Polarity:** Polymers that are similar in structure, or more generally, similar in polarity are less likely to repel each other and more likely to form miscible blends [17, 18]. Diverging polarities generally produce immiscibility.

**Specific group attraction:** Polymers that are drawn to each other by hydrogen bonding, acid-base, charge transfer, ion-dipole, donor-acceptor adducts or transition metal complexes, are less common but when such attractions occur, they are very likely to produce miscible blends [19-21].

**Molecular weight:** Lower molecular weight permits greater randomization on mixing and therefore greater gain of entropy which favors miscibility [22]. More surprisingly, polymers of similar molecular weights are more miscible while polymers of very different molecular weight may be immiscible, even if they have the same composition.

**Ratio:** Even though two polymers appear immiscible at a fairly equal ratio, it is quite possible that a small amount of one polymer may be soluble in a large amount of the other polymer, as understood in conventional phase rule. This consideration is extremely important in natural compatibility.

**Crystallinity:** When a polymer crystallizes, it already forms a two phase system with important consequences for practical compatibility. In a polymer blend, when a polymer crystallizes, this adds another phase to the system. If both polymers in a blend crystallize, they will usually form two separate crystalline phases. However, it is quite rare for the two polymers to co-crystallize in a single crystalline phase [23].
1.1.5. Practical compatibility in polymers blends:

Polymer blends have commercial importance because they offer properties, or a balance of properties not available in a single polymer. These properties depend very much on the microstructure of the blend.

Homogeneous blends:

When two polymers are completely miscible down to the segmental level, they form a single homogeneous phase and the properties are generally proportional to the ratio of the two polymers in the blend [24, 25]. This gives the compoundinger quick and economical control over the balance of properties for different applications.

Phase rule, morphology and phase stability:

When the two polymers are immiscible, phase rules explains quantitatively the extent to which they separate and the extent to which each phase is actually not pure polymer A and pure polymer B, but rather a solution of B in A and a solution of A in B. Generally the major phase will form the continuous matrix and control most properties, while the minor phase will form dispersed microdomains and contribute certain specialized properties to the blend. The less viscous phase tends to form the dispersed domains.

The structure of dispersed domains is referred to as the morphology. The simple shape of a dispersed domain which is trying to minimize its surface energy is spherical and most dispersed domains appear in this form. Generally, increasing attraction between phases tends to decrease the size of the spheres and increase practical compatibility. With increasing concentration of the minor phase, the dispersed domains may tend to become rod like and at fairly equal concentrations, the two phases may become lamellar. Another factor in morphology is shear flow during melt processing which tends to elongate spherical domains into plate like or fibrillar form. Such non-spherical morphology is generally believed to have important effects on practical properties.

Kinetics of phase separation and morphology formation are slowed down by the entanglement of large polymer molecules and the high viscosity of them.
While mechanical shear, temperature and chemical environment may change the size and shape of the dispersed domains, the system tends to revert to thermodynamic equilibrium over a period of time. This creates problems with the stability of polyblend morphology and properties.

**Interface and interphase:**

If two polymers repel each other so much that they separate into phases, the interface could be very weak and fail under any kind of mechanical or thermal stress. It is true that most polymer pairs form blends that fail under stress, have generally poor properties and are therefore defined as incompatible blends. Compatible commercial polyblends must therefore have a strong interface that permits successful stress transfer across it. Many theorists believe that a thin sharp interface creates steep property gradients which fail under stress whereas compatible polyblends must have a broad gradual transitional region, which modulates property gradients and has the ability to resist stress. They refer to this transitional region as the interphase.

**1.1.6. Compatibilization methods:**

Most polymer mixtures are not only immiscible but are also mechanically incompatible. If useful properties are to be achieved, compatibilization methods must be employed for these blends. In fact, many commercial polymer blends utilize a variety of compatibilization approaches to achieve the desired property balance. Examples include very incompatible combination such as polyolefins and polyamides. Generally, compatibilization methods involve an interface agent that lowers the interfacial tension between the components leading to a more uniform blend with smaller particle dimensions. The interfacial agent allows for improved mechanical compatibility by achieving improved interfacial adhesion between the phases. The interfacial agent can be considered a polymeric “surfactant” that concentrates at the interface and stabilizes the morphology. This stabilization prevents the coalescence which is one of the major problems in achieving small particle size dispersions by shearing uncompatibilized blends.
1.1.6.1. Introduction of specific interacting groups:

Incorporation of minor amount of specific interacting groups in polymer blends may not lead to miscibility but could be employed to improve the dispersion and mechanical properties. A generalized example of this approach would be to attach a small amount of a proton acceptor to one component and a proton donor to the other component of the blend. An early reference to utilization of this approach involved grafting minor amounts (0.5 wt. %) of an acidic or a basic monomer to components of a polyolefin blend (e.g., PE/PP) to yield improved mechanical compatibility [26].

Minor incorporation of highly interacting groups employed in polymer blends close to miscibility will expectedly shift the phase behavior from immiscible to miscible. Cases where the polymer blend components are highly immiscible will generally not show miscibility but will exhibit improved dispersion (lower phase dimensions), accompanied by strength, ductility and toughness increases.

Poly(vinyl alcohol) (PVOH) and polyethylene are highly immiscible. Introduction of modest amounts of vinyl amine groups into PVOH and acrylic acid groups into polyethylene leads to a significant improvement in the mechanical properties as well as partial miscibility and homogeneity leading to transparency [27].

1.1.6.2. Compatibilization through in-situ polymerization:

One of the important methods for compatibilizing polymer blends involves in-situ polymerization, where covalent bonding between the constituents can result in graft or block copolymers allowing for interfacial stabilization. Impact polystyrene is a specific commercial example where this concept has been very important. The polymerization of styrene in the presence of an unsaturated rubber (e.g., polybutadiene) allows for graft copolymer formation along with rubber crosslinking. The resultant phase separated rubber particles yield toughening of the brittle polystyrene matrix [28].
1.1.6.3. Ternary polymer addition (Non-reactive):

The addition of a ternary polymeric component to a binary blend of immiscible polymers has been employed in many cases to yield improved dispersion and properties. The concept involves the choice of a polymer with good interfacial adhesion to both components and interfacial tension values that will allow for concentration at the interface of the binary mixture. In essence, the ternary polymer exhibits “surfactant” – like properties and stabilizes the interfacial area, allowing for smaller particle size and improved ability to transfer stress across the interface.

Non-reactive ternary polymer systems include random copolymers, graft copolymers and polymers offering either miscibility or good interfacial adhesion between the blend components. One of the primary examples of ternary polymer addition involves the compatibilization of polystyrene with polyolefins employing styrene-hydrogenated diene-styrene ABA block copolymers.

Random copolymer addition to binary blends involving copolymers with structural units equal or similar to the blend components or with specific interacting groups capable of non-reactive interaction with one of both the blend components comprises another ternary polymer addition approach.

Graft copolymer addition with the graft copolymer consisting of a main chain of one component and the graft of the other component of the blend on the main chain provides an effective ternary polymer addition method.

1.1.6.4. Reactive compatibilization:

The area of compatibilization receiving the most interest for combining highly immiscible polymer blends into useful compositions with good mechanical compatibility is reactive compatibilization. The concept involves the introduction of a reactive site onto a polymer chain identical or similar to one blend component capable of reacting with the other polymeric component. The resultant graft copolymer will concentrate at the interface and reduce the interfacial tension, yielding improved dispersion, domain size reduction and improved mechanical properties over the binary blend. A variation of this method can involve the addition of a polymer miscible with one component and capable of reacting with
the other component to form a graft copolymer. A specific case of this variation could be a polystyrene copolymer containing minor amounts of maleic anhydride blended with PPO/PA6. The resultant PS-g-PA6 copolymer will concentrate at the interface as the PS chains prefer to be in the PPO phase.

One of the primary methods of reactive compatibilization is to utilize maleic anhydride grafted onto polyolefins or as a monomer in styrene co- and terpolymers. Maleic anhydride (MA) can react with the amine end groups of polyamides as well as the hydroxyl end groups of polyesters to yield the desired graft copolymer necessary for compatibilization. Acrylic acid can be employed as grafts or in copolymers to yield similar results. Oxazoline functionalized polymers can react with either amine or carboxylic acid end groups of polyamides or acid end groups of polyesters. Isocyanate groups incorporated as grafts or in copolymers can react with amines, carboxylic acids or hydroxyl containing polymers. Epoxy group incorporation via glycidyl methacrylate (GMA) containing copolymers or as grafted side groups can react with amine, carboxylic acid or even with hydroxyl containing polymers. Each of these systems can be grafted to polyolefins or unsaturated polymers by free radical grafting techniques employing a peroxide.

1.1.6.5. Crosslinking between phases:

Another method of compatibilization involves crosslinking between the phases of a phase separated system. This method is employed in one of the most common of commercial polymer blends, i.e., elastomer blends utilized in tire construction. In order to achieve the proper balance of properties for tire applications, crosslinked blends of phase separated elastomers are often employed. Sulfur (or peroxide) crosslinking will lead to covalent bridges between the phases, thus assuring proper translation of mechanical stress from one phase to the other.

1.1.6.6. Block copolymer addition:

Block copolymers with block compositions equal (or similar) to the components of a polymer blend can be utilized to compatibilize the blend. The block copolymer will concentrate at the interface and allow for improved adhesion
between the phases. The phase behavior of ternary blends based on two homopolymers and a block copolymer containing both components has been reviewed by Hudson and Jamieson [29]. The compatibilization aspects of block copolymers have been reviewed in a book by Datta and Lohse [6].

One of the primary examples of compatibilization involves the styrene/ethylene-butylene/styrene (SEBS) ABA block copolymer addition to polystyrene and polyolefins (PP, PE). PS/polyolefin blends exhibit poor mechanical properties that can be significantly improved with the addition of low levels of the SEBS block copolymer. The addition of SEBS to LDPE or HDPE/PS blends leads to a large decrease in the domain size of the dispersed phase [30, 31].

1.1.6.7. Polymer-polymer reactions:

Interchange reactions between different polymers can lead to compatibilization and often to miscibility between polymers that are typically phase separated. A primary example involves ester interchange between polymers e.g., polyester/polycarbonate blends. Melt mixing promotes ester exchange, leading to block copolymer formation and a transition from a phase separated blend to a miscible blend [32].

1.2. Thermoplastic elastomer (TPE):

A new horizon to the field of polymer science and technology was unfurled in the late 1950 [33] when polymer scientists were successful to impart both thermoplastic character and elastic character of a crosslinked elastomer in a single material by proper choice of polymer blend members and applying some innovative technique of blending. This led to the birth of TPE.

A TPE is a rubbery material with properties and functional performance similar to those of conventional vulcanized rubber at ambient temperature, yet it can be processed in a molten state as thermoplastic material at elevated temperature. They do not need to be vulcanized during fabrication into end products. Thus they offer a substantial economic advantage with respect to fabrication of finished parts. Most of the TPEs meet the standard ASTM D 1566 [34] definition of a rubber because (i) they recover quickly and forcibly from large
deformations (ii) they can be elongated by more than 100 % and (iii) their tension set is less than 50 %.

1.2.1. Classification of thermoplastic elastomer (TPE):

TPEs can be divided into two groups, multi-block copolymers and blends. The members of the first group are copolymers consisting of an elastomeric block and a hard block. Styrene block copolymers (TPE-S) exhibit a wide range of applications accruing from the properties such as hardness, grip and rebound. Polyester block copolymers (TPE-E) exhibit good mechanical properties until 160°C, resistance to oil and fat as well as high polarity providing the ability to be glued and varnished. Polyurethane/elastomer block copolymer (TPE-U) is a classical TPE showing very good mechanical properties and high resistance to wear. Polyamide/elastomer block copolymers (TPE-A) can be compared to both previous groups with respect to their mechanical properties. TPE from the polymer blends can be divided into TPE-O with an uncrosslinked rubber phase and TPE-V with a crosslinked rubber phase.
1.2.2. Thermoplastic vulcanizate (TPV) and dynamic vulcanization:

In TPE-O, as the rubber phase exists as uncrosslinked state, they are preferably used at lower temperature without exposition to high mechanical stress. For many end uses, the polymeric material, needs to have more elastic property, the favorable morphology should remain during the fabrication of the material into the finished product and in service life. Because of these requirements for the ideal case, the usual methods for preparing elastomer – plastic blends are not sufficient. These requirements are met, if the elastomer is present as compatibilised and as finely divided crosslinked particles dispersed in relatively small amount of plastic matrix.

The best way to produce TPE compositions comprising vulcanized elastomer particles dispersed in melt-processable plastic matrices is by the method called “Dynamic Vulcanization”. It is the process of vulcanizing an elastomer during its melt mixing with another plastic.

1.2.3. Improvements in different properties achievable in TPV:

Dynamic vulcanization is a route to new TPEs that have many properties as good or even, in some cases, better than those of elastomeric block copolymers. Thus, new, improved TPEs can be prepared from the blends of existing polymers. This technology has led to a significant number of new TPE products commercialized during the last half of the 1980. There is much commercial interest in dynamic vulcanization since the introduction of the proprietary products (e.g., santoprene) prepared by dynamic vulcanization of blends of olefin rubber with polyolefin resin. If the elastomer particles of such a blend are small enough and if they are fully vulcanized, then the properties of the blend are greatly improved. Examples of the improvements are as follows:

- Reduced permanent set.
- Improved ultimate mechanical properties.
- Improved fatigue resistance.
- Greater resistance to attack by fluids.
- Improved high temperature utility.
- Greater stability of the morphology in the melt.
- Greater melt strength.
- More reliable thermoplastic fabricability.
In short, dynamic vulcanization can provide compositions that are very elastomeric in their performance characteristics. These TPV compositions can be readily fabricated into finished parts in thermoplastic processing equipment. Because of the surprisingly beneficial effects of dynamic vulcanization, it opened a broad new field of TPE research.

1.2.4. Superiority of TPV to block copolymer type TPE:

In some respects, TPEs made by dynamic vulcanization can outperform block copolymer type TPEs. This is because the particulate elastomeric domains are comprised of fully vulcanized elastomer. As a result, the TPVs can perform well with respect to hot oil resistance, compression set (at elevated temperature) and high temperature utility. A factor contributing to the greater high temperature utility is that during fabrication of the finished product, many of the vulcanized rubber particles physically interact with one another to form “network” of vulcanized elastomer. When scrap is reground and reworked in the melt, the clusters of touching, loosely bound aggregates of particles disintegrate and melt processability is restored.

1.2.5. Some technical conditions for synthesis of technologically useful TPV:

TPVs have been prepared from a great number of plastics and elastomers. However, only a limited number of elastomer-plastic combinations give technologically useful blends, even after dynamic vulcanization. The best elastomer-plastic TPVs are those in which (i) the surface energies of the plastics and elastomers are matched, (ii) the entanglement molecular length of the elastomer is low and (iii) the plastic is at least 15% crystalline. Now it has been found that TPEs with good strength related properties can be prepared by dynamic vulcanization of technologically compatibilized blends. Technological compatibilization of the blend (before it is dynamically vulcanized) is brought about by the presence of a small amount of compatibilizing agent in the blend. The compatibilizing agent may be a block copolymer containing segments similar to each of polymers that are to be compatibilized or it may act as a coupling agent between the polymers by entering into some specific chemical interaction with the
member polymers. The compatibilizer may act as a macromolecular surfactant and its presence during mixing, permits the formation of very small particles of vulcanized rubber.

1.2.6. Advantages & disadvantages of TPE:

TPEs have both advantages and disadvantages in their practical use over conventional vulcanized rubbers.

Advantages:

(i) Have typical elastic properties of vulcanized rubber but recyclable. Scraps can be recycled and reused without significant deterioration in performance.

(ii) Require little or no compounding, with no need to add reinforcing agents, stabilizer or cure systems. Hence, batch-to-batch variation in weighting and metering components are absent, leading to improved consistency in both raw materials and fabricated articles.

Processing of TPE does not involve any vulcanization step. The flow chart given below shows a common processing scheme for vulcanized rubbers and for TPEs.

a) Vulcanized Rubber

Gum rubber
+ Filler
+ Other chemicals
Mixing
Shaping
Vulcanization
Scrap
Scrap
Finished product

b) TPE

Thermoplastic rubber
Shaping
Finished product
Recycling of scrap
(iii) Properties can easily be manipulated by changing the ratio of the components.
(iv) TPEs can be easily colored.
(iv) Processing of TPE consumes less energy and closer and more economical control of product quality is possible.

**Disadvantages:**
(i) TPEs soften or melt at elevated temperature above which they lose their rubbery behavior.
(ii) TPEs show creep behavior on extended use.

### 1.2.7. Preparation of TPV from elastomer – plastic blends by dynamic vulcanization:

Polymer blends, in general, have been prepared commercially by melt mixing, solution blending, or latex mixing. Elastomer-plastic blends of the type discussed here, containing rather large amounts of elastomer, have generally been prepared by melt mixing techniques. Melt mixing avoids problems of contamination, solvent or water removal, pollution hazards thereto etc. In general, Banbury mixers, mixing extruders, and the newer twin-screw mixers are suitable for melt mixing elastomer with plastics.

The dynamic vulcanization process has been applied to many elastomer-plastic combinations. It can be described as follows.

Elastomer and plastic are first melt mixed, usually in an internal mixer. After a well-mixed blend has been formed, vulcanizing agents (curatives, crosslinkers) are added. Vulcanization then occurs while mixing continues. The more rapid the rate of vulcanization, the more intense the mixing must be carried out in order to ensure good fabricability of the blend composition. It is convenient to follow the progress of vulcanization by monitoring mixing torque or mixing energy requirement during the process. After the mixing torque or energy curve goes through a maximum, mixing can be continued somewhat longer to improve the fabricability of the blend. After discharge from the mixer, the blend can be chopped, extruded, palletized, injection molded, etc.
1.2.8. Morphology development:

During dynamic vulcanization generally thermoplastic matrix material as well as a rubber component are blended in an extruder resulting in a, so called, co-continuous blend morphology. By means of a second opening a crosslinking agent can be added into the extruder.

During the crosslinking of the rubber phase the viscosity of the rubber increases causing the blends’ viscosity ratio to increase, since the viscosity of the thermoplastic matrix remains the same. The shear stress causes rubber phase to fall apart into fine dispersed rubber particles in a thermoplastic matrix. The formation of the characteristic matrix-particle morphology is essentially influenced by the kinetics of the vulcanization and the resulting crosslinking density of the rubber phase.

If the crosslinking density of the elastomeric phase is very poor, the rubber phase will be able to undergo large deformation and remains co-continuous. If on the other hand the crosslinking density is too high the rubber phase can only be deformed under shear stress without rupturing apart. Therefore an optimum of crosslinking density of 10 to 20 x $10^5$ mol/cm$^3$ has been suggested [35].

1.2.9. Characteristics of elastomers and plastics for correlations with blend properties:

Properties of elastomer-plastic blends have been correlated with various properties and characteristics of elastomers and plastics as described below.

*Dynamic Shear Modulus:*

This property was taken as a measure of stiffness. It was selected rather than Young’s modulus because of convenience. When considering such widely varying materials as elastomers and hard plastics, it is difficult to find a convenient test condition (rate of loading) appropriate for both elastomers and plastics. The shear moduli of the hard and soft phases (along with elastomer-plastic proportions) were correlated with shear moduli of blends.
**Tensile strength of the hard-phase material:**

This property was considered because it represents a limit for the strength of the elastomer-plastic blend. Yield stress rather than stress at break was used as tensile strength for crystalline materials since breaking occurs only after necking and drawing. Generally, the elastomeric blends do not exhibit drawing – necking behavior.

**Crystallinity:**

The reasons for considering crystallinity were empirical; however, interesting correlations between hard-phase crystallinity and certain blend properties have been obtained.

**Critical surface tension for wetting (γ<sub>c</sub>):**

This parameter (γ<sub>c</sub>) was originally used as an estimate of polymer surface energy by Zisman [36]. It was estimated by determining contact angles of various liquids against a given polymer surface. The contact angles were then plotted as functions of the surface tension of the test liquids and the surface tension of liquid corresponding to an extrapolated contact angle of zero was taken as the critical surface tension for wetting (or spreading). At one time, it was believed that γ<sub>c</sub> was approximately the surface tension γ<sub>s</sub> of solid polymer. At any rate, the difference between the critical surface tension for wetting (for the elastomer and the plastic) should be a rough estimate of the interfacial tension between the elastomer and plastic during melt mixing. Interfacial tension is a factor that determines, at least in part, the droplet size of one liquid dispersed in another [37]. Lower surface tensions give smaller droplets (which should result in smaller particles of one polymer dispersed in the other after mixing and cooling).

The interfacial tension between two immiscible monomeric liquids is approximated by the difference between the two surface tensions. Unfortunately this is not the case for polymers. However, there is a hypothetical surface tension γ<sub>x</sub>, which is characteristic of each polymer listed in Wu’s review of interfacial tension between molten polymers [38].
If the value of $\gamma_x$ for one polymer is subtracted from that of the other, the interfacial tension is estimated fairly reliably. The hypothetical values $\gamma_x$ correlated well with $\gamma_c$. It is also interesting that the critical surface tension $\gamma_c$ for wetting correlates with solubility parameter and that differences between solubility parameters ($\sigma_1 - \sigma_2$) of the polymers of a two-phase system correlate with interfacial tension. Indeed, Helfand and Sapse [39] have given a theoretical basis for this.

From all of this we conclude that $\Delta\gamma_c$, the difference between critical surface tensions for wetting of each of the two polymers, may be at least a qualitative estimate of the interfacial tension $\gamma_{12}$. The lower the difference $\Delta\gamma_c$, (which we sometimes call the surface energy mismatch), then, the smaller should be the particles of one molten polymer dispersed in the other. Also a low surface energy mismatch should give better wetting, better interfacial adhesion, and increased diffusion of the polymer across the interface.

**Critical entanglement spacing ($N_c$):**

The critical entanglement spacing $N_c$ is defined as the number of polymer chain atoms that corresponds to a molecular weight sufficiently large for entanglements to occur between molecules of undiluted polymer. It has been measured as the molecular weight where the slope of a plot of log viscosity vs log molecular weight changes from 1.0 to 3.4, the change being associated with intermolecular entanglements.

The reason for considering entanglement spacing as a parameter to correlate with blend properties was empirical. It was found that dynamically vulcanized elastomers that have low values of $N_c$ gave the higher quality blends with plastics [40].

It has been observed that, when polymers are blended together, fibrous structures appear which then break up into polymer droplets [41, 42]. We believe it likely, that polymers whose molecules are more entangled might be drawn into finer “fibers” during the early phase of mixing, to give emulsions of polymer droplets of smaller size. Of course, after dynamic vulcanization, these droplets would become very small vulcanized rubber particles.
Another explanation could be that a tendency for entanglement might promote adhesion, if some of the entanglement occurred across the interface between the molecules of the different polymers. After vulcanization and after cooling of the composition such entanglement-derived locked-in loops should improve interfacial adhesion.

It is possible to calculate values of \( N_c \) from the chemical structure of the elastomer molecules by using a modified method of Aharoni [43].

**Considering the overall view of the effects, certain conclusions can be drawn:**

(i) An increase in the crystallinity of the plastic material component improves both mechanical strength and elastic recovery.

(ii) Elastomers of lower \( N_c \) give compositions of greater mechanical integrity.

(iii) Compositions in which the surface energies of the elastomer and plastic phases are closely matched are strong and extensible.

As stated previously, matching of surface energies should give lower interfacial tensions, resulting in smaller elastomer particles that act as smaller stress concentrator-flaws, and so improve both the high strength and extensibility. Thus, based on a few characteristics of the pure elastomers and plastics, elastomer-plastic combination can be selected, with a good probability of success, to give thermoplastic vulcanizates (by dynamic vulcanization) of good mechanical integrity and elastic recovery. The best compositions are prepared when the surface energies of the elastomer and plastic material are matched, when the entanglement molecular length of the elastomer is low, and when the plastic material is crystalline. It is necessary that neither the plastic nor the elastomer decomposes in the presence of the other at temperatures required for melt mixing. Also, a curing system is needed, appropriate for the elastomer under the conditions of melt mixing.
1.2.10. Processing technology of TPV:

The processing of a rubber-plastic blend composition into a finished part is a function of the melt rheology of the composition, the temperature, and shear rate. Processing is also a function of the strength of the molten material under the strain due to its processing, that is a function of the resistance to melt fracture. The melt rheology of an elastomer-plastic blend composition is related to that of the plastic material.

At high shear rates, the viscosity-shear rate profiles are similar for both products (plastic & the TPV in question). However, at very low shear rates, the viscosity of the blend can be very high. In the case of dynamically vulcanized elastomer-plastic melt mixed blends containing high level of elastomer, the viscosity can approach infinity when the shear rate approaches zero (presumably due to cured elastomer particle-particle interference). Under the conditions of melt extrusion, the molten material undergoes rapid flow in the die. Then, as the material passes out of the die, the rate of deformation drops to zero, and, since the viscosity approaches infinity, little or no die swell is observed. The dimension of extrusion profile of such materials are thus easily controlled. This shows that the melt viscosity of an elastomer-plastic blend is highly shear rate sensitive. The viscosity of this type of blend is relatively temperature insensitive. In processing certain elastomer plastic blends by flow techniques such as extrusion and injection molding, shear rates should be kept high enough to facilitate adequate flow.

The high melt viscosity of these products can be advantageous in processing [44]. It can provide high melt integrity or “green strength” and permit the retention of shapes of parts. The high melt viscosity and low die swell are also helpful in calendaring sheet and film products. For injection molded parts, fast injection rates (under high pressure) give lower viscosities owing to the high sensitivity of viscosity to shear rate. Thus, fast injection rates facilitate rapid and complete mold filling. When the mold is filled, the shear rate is reduced to zero. This increased viscosity, which can approach infinity, enables more rapid extraction of the part from the mold. The overall effect is a faster injection molding cycle. In addition, the moderate temperature sensitivity of the viscosity of such a composition gives a “broad temperature window” for processing. It should
be noted that processing conditions vary widely with equipment mold design, specific blend compositions, etc. The best conditions for the production of a given part must be confirmed by prototype runs in factory equipment.

1.2.11. End-use application:

New techniques of melt-mixing blends of elastomers and plastics dynamically vulcanized and employing compatibilizing agents have greatly expanded the number of useful thermoplastic elastomers.

For mechanical rubber goods applications:

Caster wheels, convoluted bellows, flexible diaphragms, gaskets, seals, extruded profiles, tubing, mounts, bumpers, housing, glazing seals, valves shields, suction cups, torque couplings, vibration isolators, plugs, connectors, caps, rollers, oil-well injection lines, handles, and grips.

For under-the-hood automotive applications:

Air conditioning hose cover, fuel-line hose cover, vacuum tubing, vacuum connectors, body plugs, seals, bushings, grommets, electrical components, convoluted bellows, steering gear boots, emission tubing, protective sleeves, shock isolators, and air ducts.

For industrial hose application:

Hydraulic (wire braid), agricultural spray, paint spray, plant air-water, industrial tubing, and mine hose.

For electrical applications:

Plugs, strain relief, wire and cable insulation, jacketing, bushing, enclosures, connectors, and terminal ends.
1.3. References:


[34] ASTM 1566 “Standard terminology related to Rubber”.
http://sundoc.bibliothek.uni-halle.de/diss-online/05/05H312/t3.pdf


