CHAPTER - I

CHAPTER-1

INTRODUCTION

INTRODUCTION

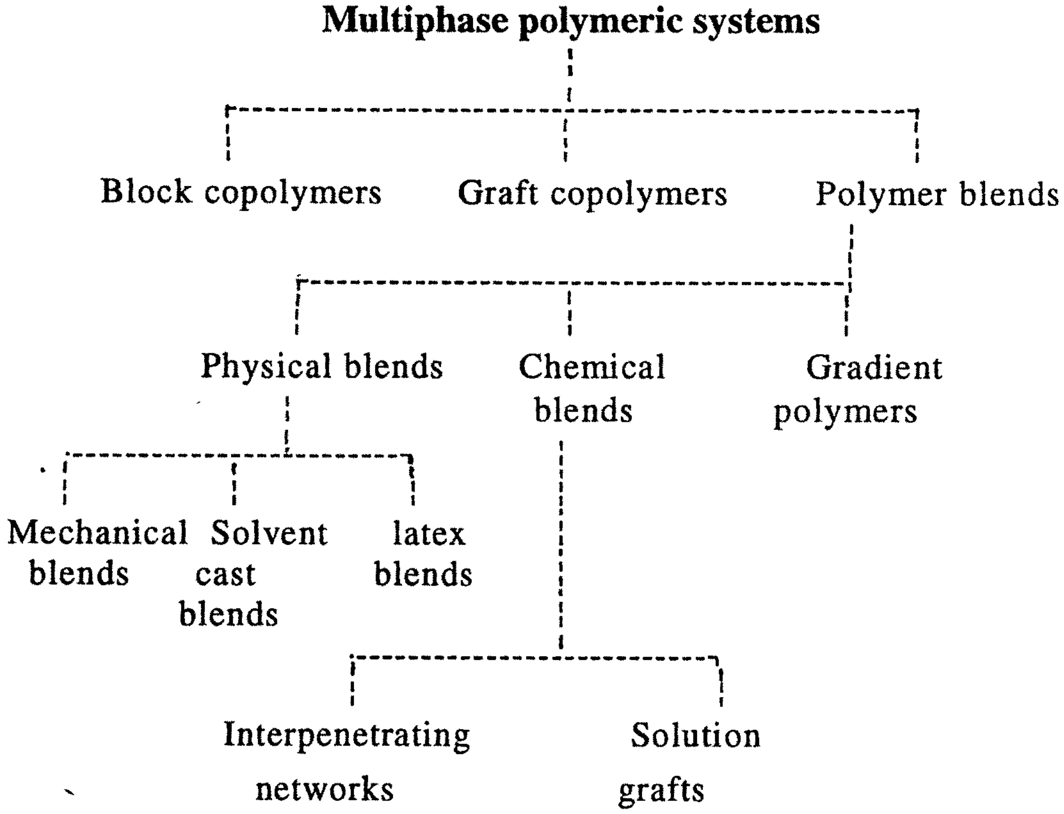
1.1 MULTIPHASE POLYMERIC SYSTEMS: GENERAL VIEW

1.1.1 INTRODUCTION

Ever since the advent of polymers, which offer definite advantages over conventional materials like metals, ceramics, wood and leather, their applications in various fields have increased enormously. The rate of appearance of new polymer types, however, has diminished over the years. In order to maintain pace with the demands of the fast developing modern science and technology, it has become very necessary to develop new polymeric materials having combination of various useful properties. This has led to widespread interest in 'multiphase polymeric systems'[1-6]. These multiphase materials may be obtained in the form of block and graft polymers and polymer blends, all of which are usually characterised by the presence of two or more polymeric phases in the solid state. Such materials are, therefore, to be distinguished from composites such as fiber and particulate filled thermoplastics and thermosets. A broad classification of multiphase polymeric systems is given below :

1.1.2 CLASSIFICATION

Multiphase polymeric systems are classified on the basis of their chain constitution. They have been defined as multicomponent polymeric systems or polyblends in which the components exist at a macromolecular level[7]. These may be classified according to the group theory concept of Sperling[8] as follows:



1.1.2.1 Polymer blends

The lack of historical perspective on the commercial development of polymer blends has led to the impression that blending is a recent development. In fact, polymer blends have been reported since the development of polymeric materials. However, only within the past decade have polymer blends reached a status ~~statics~~ to be considered as an important technology[9].

A polymer blend can be broadly defined as a mixture of two or more structurally different polymers bonded through secondary bonding and in some cases, through primary bonding forces. The most interesting feature of polymer blends is that the major component retains most of the properties, while the minor component imparts some specific properties. Thus, it is an effective technique for achieving materials with balanced combination of processing conditions, characteristic properties and cost. Due to these factors, polymer blends have gained a very important position among the materials with specific end uses.

On the basis of blending technique, polymer blends maybe further classified into two major kinds:
(1) Physical blends and (2) Chemical blends.

(1) Physical blends: The ~~P~~physical blends are prepared by mechanically mixing the components and have no primary bonding between component polymers[10]. On the basis of the nature of mixing, these may be further divided as (a) ~~M~~melt blends (b) ~~S~~solvent cast blends~~,~~ and (c) ~~L~~latex blends.

(a) Melt Blends: The simplest method of preparation of a blend is to mix the component polymers mechanically in molten state by any of the heat mixing techniques. Most often, the major component is a plastic and the minor one, an elastomer. The ease of preparation makes these blends technologically very important. Moreover, these blends offer the following advantages over blends prepared by other methods.

(i) The technique of preparation is the simplest ~~with~~ from the technological point of view.

(ii) The ingredients are readily available and are easily identified.

(iii) The blending procedure does not introduce any impurities in the systems. ? what?

(iv) It does not require removal of the extraneous solvent as it is done in solution blends. ?

(v) The degree of mixing of polymers can be attained by the balance of equipment design and temperature control which produces rheological properties required for controlling the rate and degree of mixing. x

(vi) The shear action of mechanical blending generates free radicals through polymer degradation reactions. These free radicals cause formation of true chemical grafts between the two components. The quantity and importance of such grafted material depend upon the temperature, shear-gradient and duration of blending. This phenomenon has been exploited for development of impact resistant plastics.

(b) Solvent cast blends: These blends are prepared by a solution blending x technique. In the preparation of the blends, the two polymers are dissolved in the same solvent separately. The two solutions are mixed and are brought to equilibrium. This method is generally used for theoretical studies, where behaviour of the blends is to be known at the molecular level. The advantage of this method over other methods is that it eliminates or atleast minimises the problems of incomplete mixing, chemical change caused by heat and shear gradient, color degradation and premature curing reaction. On the other hand, it has some disadvantages, since this method can only be used for ~~such~~ those polymers which are soluble in common solvent ~~as well as~~ Also isolation of the solid polymer blend requires removal of the solvent by either evaporation or coagulation which may cause heterogeneity and phase separation in the system. The use of a solvent causes the general problems associated with it such as: toxicity, flammability, environmental pollution and most important economic feasibility at industrial level.

the solvent

(c) Latex blends: If the two polymers are available in a latex form, mixing of these two results ~~into the~~ in blending at microlevel without any problems of heat or shear. The blending of two aqueous latexes is of an economic advantage and hence industrial applicability because of the absence of solvent in the latexes. The av ~~Availability~~ of two polymers in latex form and high level of impurities present in the latexes are the major limitations ~~in~~ to this technique.

(2) Chemical blends: Chemical blends involve chemical reactions. Depending upon the chemical reaction, these blends have been further divided as (a) Graft polyblends and (b) Interpenetrating polymer networks (IPN).

(a) Graft polyblends: Graft copolymerization reactions, often produce homopolymers which produce strong interfaces due to grafting reaction and become semi-compatible or compatible with graft copolymers. Such blends are called graft polyblends.

(b) Interpenetrating Polymer Networks (IPNs): Interpenetrating Polymer Networks (IPNs) can be considered as unique kind of polymer blends, synthesized by swelling of a crosslinked polymer in several monomers and polymerizing the second monomer in presence of crosslinking and activating agents in situ[11]. The two phase nature and special phase continuity aspects make IPNs interesting as toughened elastomers, impact resistant plastics, or noise and vibration damping materials.

1.1.3 FACTORS INFLUENCING POLYMER BLEND PROPERTIES

1.1.3.1 Compatibility

Two polymers will be compatible when their Gibbs free energy of mixing becomes negative, i.e.

ΔG_M = -ve value

The Gibbs free energy is given by

$$\Delta G_M = \Delta H_M - T\Delta S_M \qquad \text{———————} \quad 1.1$$

where, ΔG_M = free energy of mixing
ΔH_M = enthalpy of mixing
ΔS_M = entropy of mixing
T = temperature

Thus, the Gibbs free energy has contributions from both the enthalpy and the entropy of the constituents of the mixture. The compatibility of the blends can be considered in terms of these contributions. Since ΔS_M is always positive for polymers, for mixing ΔH_M should be negative or zero.

If two different polymeric molecules have little or no attraction for one other, ΔH_M is positive, which is an unfavorable condition for compatibility. When two large polymeric molecules are mixed, the mixing is less random due to the restricted movement of atoms resulting in~~to~~ lower ΔS_M values. Thus, the $-T\Delta S_M$ will be insufficient to overcome the positive enthalpy of mixing, resulting in~~to~~ a positive ΔG_M. As a result, the two polymers become incompatible with each other. Thus $\Delta G < 0$ is not a sufficient condition for compatibility.

According to F.H.S.[12] theory, for polymer solutions, the sufficient condition ~~then~~ is given by

$$\frac{\delta^2 \Delta G_M}{\delta \phi_1^2} = 0 \qquad \text{———————} \quad 1.2$$

where,

$$\Delta G_M = (RTV/V_r)\left[\frac{\phi_1}{m_1}\ln\phi_1 + \frac{\phi_2}{m_2}\ln\phi_2 + \gamma_{12}\phi_1\phi_2\right] \qquad \text{———————} \quad 1.3$$

where V_r is the reference volume of smallest repeat unit

V is the total volume of two polymers

ϕ_1 is volume fraction of polymer 1

ϕ_2 is volume fraction of polymer 2

m_1 is degree of polymerisation of polymer 1

m_2 is degree of polymerisation of polymer 2

γ is interaction parameter

The interaction parameter (γ) can be calculated from the solubility parameter δ of the polymer i.e

$$\gamma_{12} = (1/RT)\,(\delta_1 - \delta_2)^2 \qquad \text{——— } 1.4$$

From the equation 1.4 it is observed that lower molecular weight will permit miscibility of polymers differing widely in their solubility parameters. However, if the polymers have high molecular weight and if their solubility parameters do not differ much, then also miscibility can be achieved. Thus, the combined effects of solubility parameters and molecular weights can permit compatibility of polymer blends, within certain modest limits, at thermodynamic equilibrium.

In a few polymer pairs[13-15] where solubility parameters and molecular weights are inadequate to explain compatibility of polymer blends, homogeneity was found to result from specific group interaction, particularly hydrogen bonding and sometimes clearly identifiable complexes or adducts.

1.1.3.2 Morphology of the multiphase polymeric systems

At thermodynamic equilibrium, most of the polymeric pairs are incompatible, some are incompatible at the macroscopic or visual level, while others are incompatible at molecular and segmental levels. However, nearly all of them are incompatible at the functional group and atomic levels. From the conventional phase rule concept, it is expected that each polymer would be moderately soluble in the other even if the pair is highly incompatible. This behaviour would be manifested more at very high or very low ratios as has been proved experimentally[16]. The major polymer will tend to form a continuous matrix phase and the minor will separate out as discrete dispersed particles scattered throughout the matrix.

The separate phases are called domains. The size of these domains plays an important and decisive role regarding morphology and physical properties of the blends. The structure of the domains represents the morphology of a polymerblend. The most frequently used techniques for size and structural analysis of domains of polymer blends are electron microscopy[17-20] and small angle X-ray scattering (SAXS)[21-23].

The interfaces between two phases are of paramount importance. The lack of proper adhesion between the two components due to weak interface makes the blend "cheesy", practically a useless blend. While proper cohesion between the two components, i.e., semicompatibility at interfaces, produces blends of good practical properties.

1.1.4 BLEND CHARACTERIZATION

1.1.4.1 Density

Density is a non-mechanical property of great importance. Polymers have low modulus for their use in structural application. In many applications, the density criterion combined with strength and stiffness only / most!

gives a sound basis for comparison of polymers with different materials, such as metals and alloys.

In the case of plastic materials particularly, the density is often of a major significance as an indication of the end-use possibilities of the material. Probably the two mo~~st~~re important factors influencing the properties of a polymer, apart from its basic chemical constitution, are its average molecular weight and its crystallinity. Since the degree of crystallinity directly influences the density of the solid material, it follows that the measurement of the latter gives direct information about the former and, therefore, an important indication of the properties such as impact resistance, rigidity, short term tensile strength, softening point, low temperature brittle point, etc. Again Density dependences of blend compositions ha~~s~~ve also been reported[24-26].

1.1.4.2 Torque

The Brabender torque - rheometer has been widely used for many years to measure the consistency and processability of plastics[27,28]. Recent applications include study of poly(vinyl chloride) processability[29,30], effects of stearates on poly(propylene)[31] etc. Torque study can give ~~the~~ qualitative indications of the melt viscosity, any viscosity temperature dependence, degradation and crosslinking.

1.1.4.3 Spectroscopy

Spectroscopy can be used to investigate the structure of the molecules[32,33]. It has been proved particularly valuable in the interpretation of hydrogen bonding[34] and other interactions as applied to polymer-polymer systems. The reasoning generally followed in the application of spectroscopy is that systems of high miscibility will produce spectra showing strong deviations from an average of the spectra of the two components. The degree of deviation as a function of miscibility cannot be satisfactorily predicted before hand. This technique therefore, can only substantiate the findings from other methods for demonstrating miscibility. It does provide valuable insight into the nature of the specific interactions between the macromolecules and can often provide clues for the improvement of miscibility. ?

1.1.4.4 Microscopy

Direct visual confirmation of the prescence of two phases has been used more often than any other method as a preliminary indication of the degree of miscibility in polymer-polymer systems. The technique of scanning elect~~or~~n ron microscopy (SEM) has found a niche in phase studies. X Contrast depends on differences in surface topography or texture and this can be emphasized by breaking the specimen in its glassy state. Polymer morphology can be investigated directly by means of electron microscopy[35,36]. Has? limitations \ information

Rather brief

1.1.5 PROPERTIES OF POLYMERIC BLENDS

Why? In a homogeneous polyblend, the resulting properties should be ? intermediate between those of its constituents and more or less proportional to their weight ratios in the blend. Most of the commercial blends are made of a hard polymer of high rigidity and strength and the other polymer which is soft and rubbery[18]. The occurrence of synergism in a single property is rare. In most of the cases, the major continuous phase retains most of its characteristic properties, while the smaller dispersed phase introduces certain unique characteristics making the overall balance of properties superior to either of the components. A brief account of the individual properties is given below.

1.1.5.1 Processability.

In many cases, the processability of major polymer s is improved by X introduction of another polymer in its matrix[37]. In the case of reinforced rubbers and thermoplastic elastomers, the added polymer is a reinforced resin which has limited compatibility with rubber. In impact resistant plastics, the added polymer acts as a plasticizer to improve the fluidity of the total melt. This can provide great improvement in melt strength and ductility which may be used in blow moulding, thermoforming and postforming operations such as stretching, forging and punching.

The development of thermoplastic elastomers in the last decade has solved or eliminated the problem of rubber processing. Furthermore, the thermoplastic elastomers have also been used in the development of impact resistant rigid plastic, such as high impact rigid poly(propylene) which are mostly polyblends in nature.

1.1.5.2 Performance properties

Modulus: In a homogeneous single phase system, the modulus is roughly intermediate between that of its components depending upon the ratios of the components[38,39], whereas in the multiphase polymeric system, the behaviour of modulus and composition is not simple. The major polymer phase at its high composition range forms continuous matrix and decides the modulus of the polyblends. But at some intermediate range, where both components are present in fairly equal amounts, a sharp transition takes place. Thus, it is possible to get an insight into the effect of relative amounts of the reinforcing agent upon the modulus of the continuous matrix by using the two polymers of significantly different modulus. ~~But~~ However, the behaviour largely depends on the molar ratio and choice of polymers[40].

Strength: The relation between the ultimate strength and polymer blending has been encouraging[4]. The yielding and drawing phenomena have been observed in many polymeric alloys. There ~~has~~ have been extensive studies in the literature on the morphology of blends. ~~But~~ However, the practical strength data for different commercial polyblends, to establish a relationship between ultimate strength properties and blending, are limited.

Impact Strength : The greatest exploitation of the multiphase polymeric systems has been ~~done~~ in the development of commercially successful impact resistant rigid thermoplastics such as high impact resistant poly(styrene) (HIPS), acrylonitrile butadiene styrene copolymers (ABS), rigid PVC and toughened polyolefins. Generally, if the rubbery phase is in moderate concentration, (2 - 20 %) when dispersed throughout a rigid glassy thermoplastic matrix, a significant improvement in impact strength is obtained without any major sacrifice in other mechanical and thermal properties[6,41,42].

Heat Deflection Temperature (HDT): The heat deflection temperature indicates the continuous service temperature. It can be considered as the upper temperature limit at which the material can support the load for appreciable time. The increase in HDT is mainly due to increase in modulus of materials. It denotes the maximum temperature at which the polymer can be used as a rigid material. It is a very practical and important property of polymeric materials[41].

Hardness : Hardness is defined to be ability of a body to withstand the introduction into its surface layers of foreign bodies[43]. It depends on the properties of the material and on the shape of the indentor. The methods used to determine the hardness of plastics are similar to those used to determine the hardness of metals.

1.1.5.3 Thermal properties

Logic

The only difference between the rigid plastic and the soft rubber is the

Tg at which molecular mobility appears. Tg mostly decides the workable temperature range of a system. Thus, polymer blending of two entirely different materials each having ~~two Tgs~~ its own Tg may have an effect on the thermal properties of the resultant polyblend. In a homogenous single phase system, the transition occurs at some intermediate temperature which again depends upon the relative amounts of the components. ~~But,~~ However when blends form a two phase system, ~~it~~ they usually ha~~s~~ve two Tg's corresponding to ~~its~~ the constituents. The plateau between these two Tgs defines the useful temperature range for each multiphase polymeric system. Thus, polymer blends often have a more workable temperature range than homopolymers. The level of the modulus plateau depends upon the concentration and continuity of the two phases and also on the nature of the material whether it is an impact resistant thermoplastic or a thermoplastic elastomer.

No

~~The~~ Thermal stability studies on the multiphase polymeric systems have not received much attention[44]. In some cases[45], the component of high temperature stability may retain its integrity and control the thermal stability of the sample according to its own limit even though the less thermally stable material has failed at a considerably lower temperature. In other cases[45], the less stable component may initiate degradation of the entire sample.

Flammability of a polymer is sometimes reduced drastically considerably by blending it with a second flame retardant polymer. For example, the flammability of ABS is reduced by blending it with PVC. Similarly, chlorinated polyethylene is blended with polyethylene to improve its flame retardency particularly for wire and cable insulation.

1.2 IMPACT RESISTANT MULTIPHASE POLYMERIC SYSTEMS OF POLYVINYL CHLORIDE

1.2.1 INTRODUCTION

In ~~the~~ industrial practice, the blending of various polymers has an important effect on the balance of their properties such as the impact strength and rigidity in impact resistant plastics and the flexibility and the strength in elastomers. ~~The~~ Blending also affects other important mechanical properties such as modulus, strength, lubricity and abrasion.

As mentioned earlier, the concept of the multiphase polymeric systems has mostly been employed in the development of either impact resistant rigid plastics or reinforced rubber and thermoplastic elastomers. In both the cases, the continuous phase of the major component retains most of its characteristic properties in the final product while the minor dispersed phase introduces certain unique properties in the polymer blends.

Polyvinyl chloride has been chosen for the present study as the major component and an attempt has been made to develop PVC blends having useful combinations of various physical properties.

Significance of Polyvinyl chloride Polyvinyl chloride (PVC) was first prepared in the laboratory over a hundred years ago. Due to its inherent

The references in this section don't include even recently recent work. It they scan instability, the commercial applications of the polymer could only be developed after the development of effective means for its stabilisation. PVC started to gain commercial significance in the late thirties and since then has continued to gain importance. PVC compositions have competed with and successfully displaced such materials as metals, wood, leather, rubber, cellulose and other natural and synthetic polymers, textiles, conventional paints, glass and paper. The manufacture of wire and cables, resilient flooring, and gramophone records represent a few examples where production was revolutionized by the commercial advent of vinyl chloride resins.

Today, PVC is commercially one of the most important thermoplastics in the world. It is the second largest volume thermoplastic used in the United States and is the lowest priced among the five leading plastics. The low cost of PVC and its versatility are the major reasons for its large share of the plastic market.

PVC is a brittle, hard and semicrystalline polymer in its virgin state. It has many useful properties such as resistance to ageing, good rigidity, flame retardence, reasonably high tensile strength and high chemical resistance. But it suffers from low impact strength, low thermal stability and poor processibility. PVC has been modified for improving its mechanical properties in general and impact strength in particular by the following techniques[46].

This needs to
be brought up todate.
The references are somewhat
heavily dated.

1. Improving PVC itself through polymerizations during its production process.
2. Improving PVC itself through chemical modifications during its production process.
3. Improving blending technology to incorporate new chemical/ polymeric ingredients as modifiers into PVC.
4. Improving the processing machinery or technology.

Refs are nd

Due to technological and economic constraints, the emphasis of late is to create new polymeric materials by compounding commercial polymers with multipurpose additives, pigments, fillers, reinforcing agents and blending with other polymers. Hence polymer alloy/blending are attracting keen attention for property modification. The modification of PVC should be done in such a fashion that it offers an economic and practical approach for having the improvement of impact strength, processibililty and thermal stability without sacrificing its other useful properties.

Refs

1.2.2. STRUCTURAL REQUIREMENTS FOR MODIFYING IMPACT STRENGTH.

Rosen[47] has reviewed the requirements for attaining good impact strength in a rigid glassy polymer ~~and~~ they are:

a) The glassy polymer must be made heterogeneous by introducing a rubbery material into its matrix[48,49].

b) The rubber phase must act as a dispersed phase and its size must be regulated carefully[49-52].

c) The good adhesion between the continuous phase and dispersed phase is very ~~much~~ essential[50-54].

The impact resistance improvement of PVC depends on the extent of compatibility (degree of heterogeneity) of the modifiers with its matrix, which regulates the amount of the rubbery phase with PVC and causes insufficient adhesion and less dispersion of rubbery phase for practical utility. Although, too much compatibility gives sufficient adhesion between the two phases, the heterogeneity of the blend reduces to molecular level which results into the plasticization of the system and high impact strength is obtained at the expense of the elastic modulus and other properties[54-57].

Thus, only limited compatibility of rubbery phase with PVC is required for improving impact strength without much affecting the other beneficial physical and chemical properties of PVC.

1.2.3 THEORY OF IMPACT MODIFICATIONS

The impact resistance of a material may be improved by changing its character from brittleness to ductility. Thus, the structural phenomenon governing the transition from brittleness to ductility are the main points of the "Impact Modification Theory".

only earliest!

One of the earlie~~st~~r mechanism[54] suggests that a crack which propagates through the glassy polymer is interrupted by the dispersed rubbery particles. This results in the absorption of energy by the rubbery particles as they are deformed during crack propagation. The theory was later on abandoned when it was demonstrated that the excess energy absorption gained by addition of rubber far exceeds ~~the one~~ that which is required to break rubber particles in the unlikely event when the rubber particles are stretched to very high elongation required for deformation.

Schmidt and Keskkula[57] have pointed out an alternative energy absorption mechanism. They proposed that the rubber particles act as stress concentrator and crack arrestor and that the energy absorption takes place due to the formation of many micro-cracks around the rubber particles. However, this theory failed to explain the increased elongation and cold drawing tendencies of rubber modified plastics.

Newman and Strella[58] proposed that the increased energy absorption in rubber modified plastics is caused by increased cold drawing of the glassy matrix which causes the absorption of more energy in the viscous flow process. Under stress, the ~~dilant~~ dilatant forces around the rubber particles produce a localized increase in the volume of the glass near them.

If the bulk free volume expansion of the strained sample is to be maintained at its usual level, the lack of volume changes in the rubber must be compensated for by an accentuated expansion of the matrix immediately surrounding the rubber particles. This results in the lowering of the Tg of the polyblend and therefore, facilitates cold flow of the glassy matrix.

The differences in modifier structure and matrix properties between modified PVC and HIPS are considerable. So a simple extension of the HIPS crazing mechanism to impact modified PVC is tenuous. However, little has been reported about the impact reinforcement mechanism in the case of PVC blends[59-62]. The most useful explanation at present for the performance of impact modified PVC would appear to be built on the Newman-Strella concept[58]. The energy absorption is typically viscoelastic with the generation of heat which raises the PVC above its glass transition temperature in the adjacent area. The performance results ~~of~~ from compositional variations in impact modifiers confirm the viscoelastic concept and temperature versus impact studies confirm the effect of generated heat[63].

x

x

In summary, although much is still unknown about the mechanism of toughening of plastics by rubber and only a few systems have been studied in detail (usually at low strain rates), several features do appear to be important. The elastomer must have a low enough Tg to remain rubbery at the loading rate concerned and to initiate a combination of crazing and shear yielding in the matrix. The concentration, particle size, and phase composition should be such that many small crazes can form and interact, or branch in the matrix, not in the rubber particle itself, and that a growing crack or craze can be diverted or branched by interaction with the rubber particles. As for the matrix, clearly even a modest degree of ductility would appear to greatly enhance the role of shear yielding rather than the less efficient crazing.

split infinitive

This is 34 years old. ?
No newer examples?

1.2.4. TYPES OF IMPACT MODIFIERS

The impact modifiers for PVC on the basis of its chemical structure and composition can broadly be classified into;

a) Polyolefins, their derivatives and copolymers

b) polyacrylate modifiers

c) rubbers and their copolymers

d) inorganics and

e) miscellaneous

Of these the first three are important and are discussed in detail below:

Polyolefins, their derivatives and copolymers. Considerable amount of work has been done on the improvement of mechanical properties of PVC in the form of grafting and blending with polyolefins, ~~its~~ their derivatives and copolymers[64-71]. This is mainly due to low glass transition temperatures, high chemical resistance, good tensile strength, better processibility and high thermal stability of polyolefins and their derivatives. The modified ethylene-propylene copolymers have been used as impact modifiers for PVC. These modifiers act either through modifying PVC under processing stages or after processing. The graft polyblends of ethylene-propylene copolymers with vinylchloride show remarkable improvement in the impact resistance. Maximum toughness is obtained at an ethylene-propylene copolymer level of 8-10% in graft polyblends. These modifiers have also been used as external impact modifiers for rigid PVC.

The main hindrance in poly(ethylene) becoming an efficient impact modifier is its total incompatibility with PVC. The problem has been solved by copolymerization of ethylene with various monomers and their mixtures. The most versatile copolymer of polyethylene used as an impact modifier for PVC is ethylene vinyl acetate (EVA)[72-79]. Various studies show that it is compatible with PVC up to the concentration level of 15%. At higher concentrations, the blends exhibit properties of plasticized PVC.

Chlorinated poly(ethylene) (CPE), among the whole class of halogenated poly(ethylene)s, has been extensively used as an impact modifier for PVC[80-82]. The sufficient compatibility of CPE for impact improvement is due to the presence of polar chlorine atoms. CPE with 25-40% chlorine content is the best impact modifier. CPE containing <25% chlorine is not compatible with PVC while CPE having >40% chlorine exhibits plasticization effects. At about 40% chlorine content, CPE has a sufficiently low Tg and low crystallinity to behave as a rubber with sufficient dispersibility in PVC to form semi-compatible blends. Graft copolymers of CPE with vinyl chloride have improved physico-mechanical properties due to better compatibility between CPE and PVC matrix as a result of the grafting and have been used as impact modifiers for PVC[83].

Polyacrylates and ~~its~~ their Copolymers. The improvement in impact strength of PVC can also be obtained by the incorporation of acrylic modifiers in PVC matrix. Mostly, acrylic modifiers are graft polyblends of various monomers, comonomers and other mixtures onto acrylic rubber latex[84-86].

The maximum impact strength can be obtained by blending these modifiers with PVC in 10-15% concentration range[84-88].

The acrylic modifiers are excellent for exterior opaque application of PVC where both the colour retention and impact strength are required.

Rubbers and their Copolymers: Most of the rubbers as such are incompatible with PVC. Hence, these are used in modified form. The important rubber based modifiers have been discussed here.

Methyl methacrylate - Butadiene - Styrene (MBS) : These modifiers are made by either grafting MMA and styrene onto polybutadienestyrene rubber or by grafting MMA - styrene comonomer onto polybutadine rubber latex. These modifiers are well studied in literature and are used commercially[89-91]. They are generally used in the concentration range of 5-15%. Majority of MBS modifiers when added to PVC cause only a moderate reduction in hardness and deformation temperature. Some of the MBS modifiers provide excellent colour clarity and impact strength. Whilst modifiers of this class can be used in opaque formulations, they are of particular interest for clear compositions as may have refractive indices in the right range to promote good clarity.

References should updated?
12 min 9 15 years

These modifiers have also been used in combination with EVA and other acrylates and their copolymers[92].

Acrylonitrile - Butadiene- Styrene (ABS) : These modifiers are widely used in opaque, rigid composition for products not required to withstand weathering. In such compositions they can give high room temperature impact resistance and improved low-temperature resistance, with relatively moderate effects on the heat distortion temperature and softening point. Commercial compounds containing ABS modifiers in substantial proportions are sometimes referred to as PVC/ABS alloys or blends.

How do you know?

ABS modifiers are the most studied modifiers[93-95]. They are prepared by dispersing a rubbery phase, composed predominantly of butadiene polymers, into a rigid phase which is composed of styrene - acrylonitrile copolymers. The rubbery phase may or may not contain styrene or acrylonitrile as a comonomer grafted onto the rubbery backbone.

The improvement in impact resistance of PVC by ABS depends upon the tensile modulus and the concentration of the ABS. ABS is well suited for the modifications of rigid PVC compounds for calendering. The improved processing characteristics and their strength conferred by ABS make it a valuable additive for the production of both extruded and calendered sheet. ABS ~~is~~ has also been successfully compounded with PVC/PVAC copolymers.

Butyl and chlorinated Rubbers : The PVC blends containing 10% of isobutylene-isoprene rubber exhibit improved impact strength[96]. Chloro-isobutylene-isoprene rubber has also been used as an impact modifier for PVC. The crosslinking of these rubbers may improve both the impact strength and processibility of PVC[97]. The graft polyblend of MMA-styrene onto poly(chloroprene)[98], chlororubber-20-gp-styrene-acrylonitrile has also been used as impact modifier for PVC[99]. Chloroprene rubber in combination with MMA and/or α-methyl styrene has also been used as impact modifier for PVC[100].

Butadiene Copolymer Modifiers : The use of certain butadiene copolymers as the impact modifiers has been known for many years. The following copolymers of butadiene have been reported as impact modifiers[101-106]; butadiene-acrylonitrile, butadiene-diethyl fumerate, butadiene-dimethyl-itaconate, butadiene-vinyl picoline, butadiene-MMA, lentadiene-2 ethyl-hexyl acrylate-g-vinyl chloride and butadiene-methacrylate. penta

~~The~~ Thermoplastic elastomers containing soft and hard segments have been used as impact modifiers[106-107] for PVC. The soft segment is generally constituted by butadiene and other monomers (styrene, MMA or their comonomers) while the hard segment is composed of mixtures of butyl acrylate or copolymers of ethyl acrylate with MMA or styrene. ?

Natural Rubber (NR), Polybutadiene Rubber based modifiers:
Epoxidized Natural Rubber (ENR) and PVC have been found to exhibit good affinity for each other giving rise to miscible and partially miscible blends at 50 and 25 mol% epoxidation levels respectively when mixed in solution[108]. A recent study ~~on~~ of the morphology of epoxy - polymer/PVC blends has shown ~~that~~ the system to be immiscible at lower concentrations of PVC (upto 10%) but better miscibility was achieved at higher concentrations of PVC[109]. ENR has also been shown to function as a polymeric plasticizer for PVC[110]. Both melt mixed[111] and solution mixed[108] blends of PVC with ENR have been reported to show a single glass transition

temparature lying between that of the participating components.

Considerable stabilization~~s~~ of PVC has been attained by incorporation of PBR. The observed stabilization has been quite reasonably explained on the basis of polar interactions within the PVC matrix[112]. Epoxidized poly(butadiene) (EPBR) has been used as a modifier for PVC, as well as chlorinated PVC[113,114]. Miscibility in such solution cast blends require~~d~~s degrees of epoxidation > 50 mol%, as in the case of PVC/ENR blends. The miscibility behaviour has been explained on the basis of polar/polar and/or donor/acceptor interaction among the acidic hydrogen atom of PVC and the oxirane ring. However, not much has been reported on the syst~~a~~ematic investigation of melt mixed PVC/PBR and PVC/EPBR blends of varying composition, encompassing the effect of the epoxidation level on thermal and mechanical properties.

1.2.5 THE PRESENT INVESTIGATION:

The ~~main~~ major drawbacks of PVC are its low impact strength, its thermal instability and ~~poor~~ low processibility. As mentioned earlier, the bulk of the effort~~s~~ in the property modification of PVC ha~~ve~~s been concerned with the performance improvement in toughness and thermal characteristics.

The objective of the present investigation was to study the effect of incorporation of high molecular weight PBR and partially epoxidized PBR into PVC matrix, on the thermal and performance properties of PVC.

It is known that addition of an elastomer to any engineering resin will improve its impact strength. High molecular weight PBR was chosen as the elastomeric phase because high molecular weight substances are expected to provide superior permanence in physical properties than their low molecular weight counterparts. In addition~~s~~, ~~C~~cis 1, 4 - PBR has a low Tg and therefore it can act as an efficient plasticizer for PVC. But PBR, being non-polar in nature, is immiscible with polar PVC. Partial epoxidation will introduce a certain degree of polarity and hence compatibility with PVC. That is why epoxy compounds are extensively used as heat stabilizers and secondary plasticizers for PVC. Considering these aspects, high molecular weight EPBR was expected to be a potential modifier for PVC. For economic reasons mechanical blending pr~~o~~edominates and therefore, various PVC blends were prepared by melt mixing.

In the present investigation chemical modification of PBR has been carried out by epoxidation. The reaction conditions have been optimised to achieve the desired level of epoxidation (5 - 25 mol%). Epoxidized poly(butadiene) (EPBR) samples have been characterized by various techniques especially to determine the degree of epoxidation. A chlorohydrin derivative of PBR has also been prepared and characterized.

Blends of PVC with PBR, EPBR (25 mol% epoxidation) and chlorohydrin containing 2.5 to 15 wt % of the rubbery phase have been prepared by melt mixing. Also PVC/EPBR blends with 90/10 composition, but containing EPBR with different epoxy content, have been prepared.

The blends have been characterized by various methods (~~C~~chemical, spectral, thermal, mechanical etc.). The modification in properties of PVC brought about by various modifiers has been compared and explained on the basis of possible interaction between the components of the blends.

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