CHAPTER-II

LITERATURE REVIEW
2.0 Introduction

The present thesis is directed towards studying the elastomer - plastomer polyblend systems made by applying interpenetrating polymer networks technology giving emphasis on mechanical, physical and morphological analysis of the IPN systems. So, the system can be considered as an IPN combination of soft (i.e., elastomer) and hard (plastomer) block. The total study was carried out with a single soft block i.e., natural rubber and two hard blocks viz., polystyrene and poly(methyl methacrylate).

In the context of studies undertaken in the present thesis, it would be worthwhile at this point to make a survey of the related literature. To have a concise and directed review we are to be confined in polymeric materials involved in studying the IPN system in the present thesis. Again, as the IPN technique is employed in preparing the polyblend under consideration, the survey will be based on Interpenetrating Polymer Networks systems.

A great number of publications can be found on IPN systems having polystyrene as one of the major components. The systems with polystyrene - polystyrene/castor oil are found to be major area of research undertaken in this class. Again, IPN systems containing polyacrylate or copolymer of acrylates or modified acrylates are also found in a wide range of research work. In this class, most of the works are based on simultaneous mode of preparing the IPN. Here also a great amount of work was done on systems containing polyurethane and polyacrylate. A considerable number of research publications can be found on IPN systems based on polyacrylate and polystyrene.
2.1 **IPN Systems Containing Polystyrene or Copolymer of Polystyrene as one of the Components**

An extensive research has been carried out taking polystyrene or its derivatives as one of the major components in different kinds of IPN systems. A few selected systems are discussed below.

2.1.1 **PS-PU/Castor oil based IPNs**

Mechanical, thermal and Morphology of topologically interpenetrating chain networks, prepared by simultaneous cross-linking of a glassy polymer (e.g., polystyrene) or a polyester, and a urethane rubber under conditions to minimise chemical interactions between the two different networks were studied. Mechanical and thermal properties were found to be superior to those of the corresponding component networks and tensile strength maximum occurred at an intermediate concentration of the two constituent networks as a result of interpenetration which was shown by an apparently higher crosslink density. In some cases there was a similar enhancement in thermal resistance as measured by thermogravimetric analysis (68). In another study (69) a series of IPNs of polyurethane-crosslinked polystyrene were synthesised under high pressure. The morphology, dynamic mechanical properties and density behavior were analysed to determine the effect of synthesis pressure on the degree of interpenetration of the component polymers. The composition of the polyurethane and polystyrene components of the IPN were fixed at 50% / 50% by wt. The dynamic mechanical behavior showed changes from the heterophase structure
to the homogeneous single phase IPNs. The degree of intermixing in systems of polystyrene or crosslinked divinyl benzene styrene copolymer and polyurethane (70) (from MD)-terminated polytetramethylene glycol, 1,4-butane diol and when crosslinking was required, trimethylolpropane) increased with increasing pressure in preparation. The relative degree of intermixing was higher for full IPNs over semi IPNs. Morphology was shown by electron microscopy to follow a similar trend. Small angle X-ray scattering of IPNs (prepared by polymerising styrene (I) with 2% divinyl benzene (II) in a polyurethane (III) swollen in a I-II mixture) was studied by Lipatov, Yu. S. et al. (71). They obtained dimensions of heterogeneous domains, thickness of the transition layer, degree of segregation of the components, diffusibility of phase boundaries, and degree of mixing of the components on the molecular level. The formation of heterogeneous structure (72) in IPN during Bz2O2-catalysed polymerisation of divinyl benzene with styrene in the presence of polyurethane is attributed to phase separation of the glycol chains from the copolymer. The polymerisation of a penetrating network is controlled by diffusion of I and II molecules to the end of the propagating chains through a relatively thick layer of matrix network. The structure of the matrix network (particularly at high I and II content) changes in the swelling stage from a homogeneous into a heterogeneous system in which the glycol solution in I-II mixture form the hard segments. At low I and II content, phase separation of the components at the polymer stage remains essentially incomplete. At medium (8.6%) monomer concentration inclusions of highly dispersed particles
of divinyl benzene styrene copolymer behave as a rigid filler in an elastic matrix. Interpenetrating networks were prepared from (25:75) - (75:25) 1,4 - butane diol - MDI - polytetramethylene glycol - trimethylene propane copolymer (I) - divinylbenzene styrene copolymer (II) combinations at high pressure and comparisons were made with the analogously prepared linear blends of 1,4-butane diol - MDI - polytetramethylene glycol copolymer and polystyrene (73). The degree of mixing increased with increasing I-II ratio. The morphology via transmission electron microscopy agreed well with the glass transition and modulus behavior. Swelling data indicated that there might be some effect of the interactions caused by the interpenetration of the I and II network.

When styrene (I) and divinylbenzene were absorbed in a castor oil based urethane polymer and polymerised in situ by UV-irradiation (74), the glass transition temperature of the products gradually merged from two distinct transitions into one broad transition at an intermediate temperature as the crosslink level of the castor oil component was increased. At low I content, the stress strain behavior was similar to that of reinforced rubber; however at high I content, elongation was increased and the yield points were well developed. Stress whitening, necking and cold drawing under tension were observed. The tensile strength and Young's modulus were enhanced when the urethane crosslinking was increased at constant I content as well as when I-content was increased at a constant urethane cross-linking level. The impact properties were optimum at NCO/OH = 0.95 for systems containing TDI polyurethane. In a different study (75), castor oil was
polymerised and crosslinked with S or 2,4-TDI to form the vulcanized and urethane derivatives, respectively. Both types were swollen in a monomer-crosslinker mixtures and a second polymerisation was carried out in situ. Polystyrene prepared in the presence of Na-ricinoleate emulsifier, was mixed with styrene, castor oil and S to produce a semi-IPN upon heating. The polystyrene phase size of the castor oil-urethane/Polystyrene interpenetrating network decreased with increasing crosslinking of the castor oil component and with increased polystyrene content. Two distinct glass transition temperatures were observed in all cases. Stress-strain results showed that some of the IPNs behaved as reinforced, highly extensible elastomers at low polystyrene levels, and as rubber toughened plastics at high levels of polystyrene or crosslinking.

Electron microscopy of IPNs of polystyrene (I) and urethane rubber based on castor oil or TDI or hexamethylene diisocyanate showed a cellular structure (76). The I domain size decreases with increasing crosslink level of rubber phase and increasing I content. The chemical structure of the diisocyanate crosslinker showed no apparent influence on the morphology of the composite. Electron microscopy of a SIN prepared by cross-linking castor oil with sebacoyl chloride and polystyrene (I) with divinylbenzene showed a complex two phase morphology dependent on the relative gelation times of the two polymers, the one gelling first being the more continuous phase (77). Stress-strain curves showed a plastic component with a well
developed yield point as well as a highly toughened elastomer. Both are tougher than the corresponding homopolymers.

The synthesis of castor oil based polyester or polyurethane SINs in bulk involve the transformation of the multimonomer solution into an oil-in-oil emulsion in which the newly formed polystyrene chains precipitate, giving rise to a dispersed phase (78). Stirring is very important in preventing layering of the reaction mixture. Components containing 10% and 40% of the elastomer component behaved as tough plastics and reinforced elastomer respectively. Devia N. and co-workers (79) also studied the morphology and mechanical properties of IPNs, prepared by polymerisation of styrene in the presence of sebacic acid - castor oil reaction products or of polymers of these products with TDI.

2.1.2 IPNs based on Styrene Butadiene Rubber and Polystyrene

L.H. Sperling and coworkers studied IPNs based on styrene butadiene rubber/polystyrene (80). The dynamic mechanical behavior of IPNs of styrene butadiene rubber and polystyrene showed distinct transitions for each polymer which was consistent with the two phase morphology revealed by electron microscopy examination. An increase in the crosslink density of the polymer formed first produced greater interaction between the two components and greater continuity of the second formed polymer phase. Room temperature yield strength and modulus decreased with increasing butadiene-styrene rubber content but increased with an increasing degree of cross-linking of the rubber phase. Tensile strength and impact tests demonstrated that the network produced toughened material and the
principle of toughening mechanism involved crazing. An optimum degree of toughness was obtained at an intermediate level of crosslinking in the first formed polymer component. In IPNs of butadiene styrene rubber and polystyrene, the component formed first formed the more continuous phase and tended to control the morphology (81). The second formed a cellular structure with the cell size determined primarily by the degree of crosslinking of the first polymer. An increase in crosslink density of the first formed polymer resulted in a fine cellular structure. The crosslink density of the second polymer has no significant effect on morphology. The networks were synthesized by swelling the crosslinked rubber with a styrene solution of 0.4% dicumyl peroxide containing varying amounts of divinyl benzene and heating four days at 50°C and 1 hour at 100°C, and dissolving uncrosslinked rubber in a styrene solution followed by thermal polymerisation.

2.1.3 Polyvinylpyridine - Polystyrene IPNs

A theoretical analysis of unsubstituted polystyrene (I) - Polyvinylpyridine (II) interpenetrating networks (IPN) showed that no additional crosslinks were developed in the swollen state. Modulus studies showed that the I network tends to dominate the mechanical properties in the bulk state. Swelling studies on ionomeric IPN as a function of pH showed a complex change on addition of NaCl, possibly due to an ionic screening effect. Electron microscopy studies showed a two phase structure. Dynamic mechanical studies supported the two phase morphology and gave evidence of significant molecular mixing between phases (82).
2.1.4 Isoprene-styrene triblock copolymer and Polystyrene IPNs

Widmaier and coworkers prepared and characterized a semi IPN based on divinyl benzene crosslinked polystyrene and poly-styrene polyisoprene three block copolymers (SIS). Anionic polymerisation technique was applied to synthesise the IPNs (83,84). In a different paper, Widmaier et al. studied physico-chemical interpenetrating networks of isoprene-styrene triblock copolymer (I) rubber with divinylbenzene styrene copolymer (II) made by anionic polymerisation, and it was found that the tridimensional structure, formed in the second stage of polymerisation, had increasingly more defects as network meshes become smaller; i.e. as the crosslink density increased (85).

2.1.5 Plant Oils and Polystyrene Interpenetrating Networks

The mechanical properties and morphologies were studied (86) for SIN-containing crosslinked polystyrene and elastomeric components based on dimer acid - crosslinked epoxidized linseed, crambe, lunaria and lesquerella oils. All the interpenetrating networks exhibited a two phase morphology. Improved impact resistance and fatigue resistance were observed in interpenetrating networks especially in the case of systems based on crambe oils. Sperling, L.H. et al studied simultaneous interpenetrating networks prepared from special functional group triglyceride oils, castor oil, lesquerella Palmeri and other wild plant oils (87). The morphology of the sample depended on the method of synthesis. The sequential IPN had smaller domains than the SIN. Modulus-temperature stress-strain and impact resistance studies of a number of compositions showed that the SIN and IPN from both
castor oil and LPO or epoxidized LPO were either tough plastics or reinforced elastomers depending on compositions. Morphology and mechanical behavior of SINs from epoxidized triglyceride oils and polystyrene was studied by Sperling, L.H. et al (88). Electron microscopy showed that two phase systems were obtained in all cases, with the morphology being dependent on the oil and the synthesis procedure. Here again, the products ranged from toughened plastics to reinforced elastomers. The polymerisation of vernonia oil, or natural triglyceride containing many epoxy groups, with sebacic acid (I) is second order with respect to I and 1st order with respect to vernonia oil (89). The polymerisation of vernonia oil with I gave polyester type soft elastomers. Styrene and divinyl benzene were copolymerised in the presence of a vernonia oil - I polymer and BZ₂O₂ at 80-140°C to form interpenetrating networks having promising properties, e.g. 50:50 composition formed a opaque white, tough elastomer. In a different study Sperling, and coworkers established that IPN systems based on vernonia oil and polystyrene have good dynamic mechanical properties (90).

2.1.6 IPNs based on Polybutadiene Rubber and Polystyrene

Sperling and coworkers studied the morphology and phase dimensions of interpenetrating polymer networks based on polybutadiene and polystyrene by small angle neutron scattering and electron microscopy (91). It was observed that an increasing crosslinking of both polymers produced a finer morphology with greater regularity (dual phase continuity) for semi IPN of polybutadiene - polystyrene and full IPN of polybutadiene and divinyl-
2.1.7 Polystyrene-Polystyrene IPN Systems

An IPN consisting of two networks, having the same chemical composition can be obtained by sequential technique. IPNs of this class are known as Millar IPNs or homo IPNs. In this subclass, crosslinked copoly(styrene-divinylbenzene) systems were investigated by Millar and Shibayama (92). Both the networks were obtained by benzoyl peroxide initiated radical polymerization. Later on in 1980, Siegfried et al (93) made a thorough investigation on this PS/PS Millar IPNs. They synthesized PS-PS IPNs in which polymer I contained 0.4% divinylbenzene. Polymer networks I and II were prepared by thermal and photopolymerisation technique respectively.

A new procedure for preparation of model polymer networks having an inhomogeneous distribution of crosslinks was developed by Kelley et al. (94). Emulsion polymerized divinylbenzene styrene copolymer microphases of uniform particle size, were swollen with styrene monomer, which was later polymerized in situ. The resulting network consisted of discrete sites of crosslinked material dispersed in an interpenetrating matrix and was suggested as a model for the molecular morphology in some epoxy networks.

2.1.8 Other Important IPN systems Involving Polystyrene/Copolymer of Polystyrene as one of the Component

IPNs containing living polymer chains were prepared by (naphthalene) Sodium initiated polymerisation of bis(triethylenep
glycol) phthalate dimethacrylate or
triethylene glycol dimethacrylate in solution (matrix network), addition of styrene and divinyl benzene, and anionic co-polymerisation of the later monomers (penetrating networks) (95). Small angle X-Ray scattering indicated differences in the degree of heterogeneity and in the size of heterogeneous regions that were ascribed to the presence of a large number of charged sites with different levels of coulombic interaction in the matrix and penetrating networks.

The effect of reacidification and annealing on the morphology of IPNs based on ionically crosslinked polymers were studied by Sperling et al. (96). In this study annealing was found to be an alternative method of inducing dual phase continuity in multi-polymer combinations. Annealing resulted in a more continuous phase morphology. The physicomechanical properties of chemically-blended thermoplastic IPNs (CBT-IPN), prepared by sequential polymerisation of styrene-1ethylene-co-butylene-b-styrene block copolymer (I) with ionomeric isoprene-methacrylic acid - styrene copolymer (II), and mechanically blended thermoplastic IPNs (MBT-IPN), prepared by melt blending of I and II were comparatively studied by Sperling, et al. (97). The CBT-IPN exhibited greater tensile strength and higher elongation at break, but lower modulus than the MBT-IPN materials of the same overall compositions. Morphology studies revealed more equal dual phase continuity or greater dual phase connectivity in MBT-IPN than CBT-IPN materials after ionomer formation.
Lipatov, and coworkers studied the microphase structure of an IPN from Oligoisoprene dihydrazinide epoxide oligomer and styrene copolymer with divinyl benzene (98). The microphase structure was investigated by small and wide angle X ray scattering and electron microscopy. Ion exchange equilibrium properties of interpenetrating sulfonated polystyrene resins was studied by Liu, Linsha, and co-workers (99). Frisch et al. studied the full interpenetrating (FIPN), pseudointerpenetrating (PDIPN) and linear blends of poly (2,6 dimethyl-1,4-phenylene oxide) and polystyrene (100). They found a single phase behavior as shown by glass transition analysis and electron microscopy. The glass transition temperatures ($T_g$) were lower than the $T_g$ (average) and corresponded with the maximum tensile strength.

2.2 **IPN systems Containing Poly-Acrylate or Copolymer of Acrylate or Modified Acrylates as one of the major Components**

An wide range of works has been done taking acrylates as one of the components in studying different aspects of interpenetrating polymer networks. Most of the works are based on simultaneous mode of preparing IPN. The following review of the related literature might be relevant in the context of the present thesis.

2.2.1 **IPN system based on mainly Polyurethane and Polyacrylate**

An enormous amount of work was done on this particular system. Therefore, it would be necessary to cover this area with somewhat greater attention. The following review concerns only a limited number of important works on this system.
Two component IPNs containing 1,4 butane diol - methylene -p-phenylene isocyanate - Niax D560 - trimethylol propane polymer and methyl methacrylate - trimethylol propane trimethacrylate polymer were prepared by simultaneous polymerisation as well as pseudo IPN containing only one crosslinked component, and blends of linear polymers (101). Phase separation was shown by electron microscopy and the phase domains were finer in IPN than pseudo IPN or blends. Frisch, and coworkers made a study on IPNs based on polyurethane and poly(methyl methacrylate) (I) (102). The maximum ultimate strength (tensile) was observed at 85% PU - 15% (I) and was due to filler reinforcing effect of the rigid I phase. The ultimate tensile strength of 75:25 PU-I IPN was higher than that of the corresponding pseudo IPN (only one network crosslinked) and the linear blend. The leathery and glassy composition did not show any reinforcement in ultimate tensile strength, indicating that the reinforcement was not directly related to interpenetration, but indirectly related by reducing the rigid phase domain sizes and increasing the adhesion between the two phases, enhancing the filler reinforcement effect similar to that observed in a carbon black filled rubber. The tear strength of the PU rich IPNs, pseudo IPNs, and linear blends were higher than that of the pure polyurethane as a combined result of increased modulus and tensile strength. Investigation on structure and thermodynamic properties of interpenetrating polyurethane network was done by Lipatov et al. (103). This investigation indicated the presence of a transition region between two phases of the component polyurethanes, in spite of the absence of chemical interaction and thermal incompatibility of the later. The investigated interpenetrating networks consisted
of a polyurethane acrylate prepared from ethylene glycol monomethacrylate propylene glycol and toluene diisocyanate and a polyurethane prepared from propylene glycol, toluene diisocyanate, and trimethylol propane. Heterophase IPNs were obtained by Klempner et al. by applying various methods involving crosslinked PU elastomer phase and acrylic copolymer glassy phase, the heterogeneity being determined by the glass transition temperature (T_g) (104). They were prepared by combining a urethane prepolymer containing a chain extender and crosslinking agent, with an acrylic copolymer (prepolymer 20-30% conversion) containing a crosslinking agent, casting between teflon lined plates, and curing for 3 hours at 130°C and 20 hours at 120°C. Djomo et al made a study on side reactions occurring in the early stages of formation of the polyurethane - poly(methyl methacrylate) interpenetrating polymer networks (105). The PU catalyst Sn(II) octate initiated polymerization of methacrylate monomers or accelerated it in the presence of the initiator AIBN. This effect did not influence the overall reaction. Light needed to be excluded in order to obtain transparent interpenetrating networks. The kinetics of formation of individual networks were investigated under conditions as close as possible to the actual preparation of interpenetrating networks. Intersystem grafting was found to be very limited. A study of the stress-strain and impact properties of polyurethane interpenetrating networks with poly(Me-methacrylate) (I) shows the expected behavior when the elastomer content is varied from 15 to 50%. For a given composition the main factor influencing the mechanical properties are the
crosslink degree of each network. The crosslink degree of polyurethane network is more important, probably because it is formed first. (106). Li, Binyao et al synthesised an IPN based on polyurethane (hydroxy terminated acrylonitrile butadiene copolymer (I) – TDI copolymer) poly(Me-methacrylate) and they examined it by dynamic mechanical spectroscopy and transmission electron microscopy (107). In a different paper (108) they studied the glass transition behavior and morphology of PU (HTBN)/PMMA interpenetrating networks. Some semicompatible IPNs were obtained by increasing the amount of the nitrile group or using chain extenders. Due to the strong interaction of polar groups in the IPN, the phase domains become finer and only a single glass transition was observed. Hourston and coworkers studied semi and full IPNs based on polyurethane-polyacrylate systems (109). Two series of semi-2 IPNs (semi IPNs in which the second formed polymer is the crosslinked component) based on polyurethane and a poly(Me-acrylate) crosslinked with divinylbenzene were prepared and investigated using dynamic mechanical analysis; sonic velocity measurements and electron microscopy. In one series, the level of crosslinking was varied to give ultratight networks. In the other, the composition was altered but the amount of crosslinking agent used was kept constant. In a different paper, Hourston et al investigated that the semi IPN showed substantial phase separation but the phase sizes were ordered of magnitude smaller than those observed for blends of the same linear polymers. The effects of the hydroxyl isocyanate ratio used in the preparation of PU, of the molecular weight
of the linear component, of the overall composition, and of the molecular weight between crosslinks in PU networks were investigated (110).

The condition of formation of IPN from castor oil polyurethane and homopolymers or copolymers of styrene - methyl acrylate and acrylonitrile at room temperature were studied using initiators composed of $Bz_2O_2$ and dimethyl aniline (111). When the weight percentage of polyurethane was higher than 50%, the IPN exhibited the behavior of an elastomer. During the formation of IPN, linear polymer and crosslinked polymer were formed simultaneously and then the former converted completely into the later. The IPN had high strength, good resilience and high resistance to abrasion and hydrolysis. A series of PU-poly (Me-acrylate) sequential IPNs containing 40% PU were prepared and characterised by Hourston et al (112). The triol/diol ratio used in the preparation of first formed PU network was changed so that the average molecular weight between crosslinks ranged from 9500 to 500 g/mol. In addition to decreasing this molecular weight, changing the triol/diol ratio alters the hard segment content of the polyurethane. As the triol/diol ratio increased, the extent of mixing increased and there was evidence of phase separation of the hard segment of the PU component at high triol/diol ratios. Dynamic mechanical properties measured at 11 Hz and -75°C to +75°C were dependent on sample homogeneity and use of Sn catalyst for interpenetrating networks based on urethane (I) - Bu acrylate - Bu methacrylate copolymer (II) blends. SINs
prepared with a Sn catalyst had a higher crosslinking density, 
a higher glass transition temperature ($T_g$), a greater rubber 
complex modulus and more transition broadening than sequential 
IPNs (SIPN) (113).

The effect of prepolymer molecular weights, crosslinking 
extent, charge groups, intentional grafts, and pseudo inter­
penetration on the morphology and mechanical properties of 
interpenetrating polymer networks (IPNs) involving polyurethane, 
acrylic polymers and copolymers, and epoxy resin had been studied 
by Frisch et al (114,115). The best strength properties were 
exhibited by the most compatible IPNs. Charged groups in the 
polymer increased interpenetration and enhanced mechanical 
properties and intentional grafting yielded similar results. A 
50:50 1,4 butane-diol-MDI-poly-tetramethylene glycol - trimethylol 
propane - copolymer (I) - ethylene methacrylate-Me-methacrylate 
copolymer (II) interpenetrating network prepared by simultaneous 
polymerisation and crosslinking at 11,000 kg/cm$^2$ and 100°C for 
24 hour had a domain structure with domain sizes 500-1000 Å 
compared to 2000-5000 Å when prepared at 60°C/1 atm. The high 
pressure network had a higher modulus and thermal stability, due 
to higher interlocking than in the low pressure network. The 
tan $\delta$-temperature plot showed a very broad polyurethane transition 
at $-40^\circ$C to $+30^\circ$C in both 50:50 and 70:30 high pressure network. 
Heating 24 hour at $120^\circ$C did not alter the shape or position of 
the $\delta$ peak (116). A series of simultaneous IPNs from 1,4 butane 
diol-MDI-polytetramethylene glycol trimethylolpropane poly­ 
urethane (I) and ethylene glycol dimethacrylate-Me-methacrylate
copolymers (II) were synthesised under high pressure (< 20,000 kg/cm²) (117,118). The morphology via transmission electron microscopy and the glass transition behaviour via dynamic mechanical analysis and DSC measurements were studied, and the effect of the synthesis pressure was evaluated. The weight ratio of I and II was 1:1, the I phase domain size decreased from 300 to 30 Å with increasing synthesis pressure from 1250 to 20,000 kg/cm². The phase continuity also changed with pressure, the I phase became continuous at low pressure, while the II phase showed continuity at high pressure. A very broad glass transition (0-100°C) was observed for IPNs synthesized under 20,000 kg/cm² and they were transparent. Synthesis and thermal properties of polyurethane, poly(butyl methacrylate) and poly(methyl methacrylate) multi component IPNs was studied by Lee, Jac Heung; et al (119). Three component IPNs of polyurethane, Bu-methacrylate ethylene dimethacrylate copolymer (I) and ethylene dimethacrylate – Me-methacrylate copolymer (II) were prepared by a combination of simultaneous and sequential polymerisation.

The physicomechanical properties of interpenetrating networks of polypropylene glycol-TDI-trimethylol-propane copolymer rubber with Me methacrylate-trimethylolpropane trimethacrylate copolymer showed that crosslinking of the second phase induced better miscibility, with the rubber network being more significant owing to its quality and the fact that it was formed first (120). Frisch et al. studied IPNs composed of MDI-poly(1,4 oxybutylene) glycol copolymer (I) and methacrylic acid – Me methacrylate copolymer (II) (121). Phase miscibility was improved and extent
of phase separation was decreased in both IPNs on increasing
the NCO/OH ratio, decreasing molecular weight of the polyol
in I, and introduction of charged groups. Increased compatibility
in full IPN and graft copolymers was observed by DSC and SEM and
was substantiated by a shift toward single glass temperature as
determined by dynamic mechanical spectroscopy. The introduction
of oppositely charged groups in two component IPN from I and
epoxyes led to improved compatibility (no phase separation) and
enhanced mechanical properties. Two and three component IPNs were
formed from polyurethane, epoxy resin and acrylic copolymers
using the simultaneous technique (122). The IPNs exhibited a
variety of morphologies and properties depending on the type of
polymer, prepolymer molecular weight, presence of charge groups
and presence of intentional grafts between the component polymer
networks. It was observed that, the presence of intentional grafts
and the presence of charge groups of opposite charge resulted in
increased homogeneity and better mechanical properties in the IPNs.

Kordomenos et al. prepared coating compositions based on
acrylic - polyurethane IPNs (123). It was prepared by mixing
crosslinked Bu-methacrylate-2-hydroxyethylacrylate-isocyanatoethyl
methacrylate copolymer (I) with Desmodur N100 - crosslinked Bu-
methacrylate-2-hydroxyethyl acrylate copolymer (II). The composi-
tions were thermally cured on substrates by radical initiators.
The coating had tensile strength 2303-4351 psi (maximum for a
60:40 blend of I and II), elongation 11-37%, Shore A hardness
76-89, lap shear strength on steel 202-784 psi. The performance
of the coating was generally superior to that of coatings from
I or II above. The morphology of the coatings, determined by SEM, confirmed the existence of interpenetrating networks. The synthesis, morphology, thermal and mechanical properties of interpenetrating polymer networks were studied using examples like - polyurethane - polyacrylate and poly(2,6-dimethyl-1,4-phenylene oxide)-polystyrene systems (124).

2.2.2 Acrylate-Acrylate Interpenetrating Polymer Networks

Sperling and coworkers studied acrylic latex interpenetrating network coating systems constrained with fibre reinforced epoxy coating for vibrational damping for noise abatement over a broader temperature range than commercial extensional damping coatings (125). The latices used were a crosslinked 25:75 poly (Ethyl methacrylate)poly Bu-acrylate interpenetrating network and a crosslinked 21:9 Et-acrylate - ethyl methacrylate copolymer - 21:49 Bu-acrylate - ethyl acrylate copolymer IPN.

Dynamic mechanical properties and stress strain behavior of IPN systems composed of poly(Et acrylate) (I) and poly(Me methacrylate) (II) were examined by Adachi et al. (126). Viscoelastic properties showed that in the process of IPN formation, Methyl methacrylate (III) is likely to first form microgels in the I network, with these microgels eventually interconnecting to form a fully interpenetrating network having microheterogeneous modular domains. The glassy II microdomains imparted a filler effect (similar to that found in filled elastomers). Semi and full IPNs of 75% II content in which the II was uncrosslinked and crosslinked respectively, were also prepared, and the
2.2.3 **IPN systems based on Poly(acrylonitrile-co-butadiene) and Polyacrylate**

Adachi et al. studied the structure and mechanical properties of sequential IPN involving poly(acrylonitrile-co-butadiene)/poly(Me methacrylate) systems. (127). Two types of IPNs consisting of incompatible nitrile rubber and PMMA as the first and second components, respectively, were prepared; one was a semi IPN in which only nitrile rubber was crosslinked, and the others were full IPNs in which both nitrile rubber and PMMA were crosslinked. Electron micrographs showed heterogeneous and fairly homogeneous structures containing a continuous nitrile rubber phase for semi and full IPNs, respectively. These structures were compatible with the mechanical properties (viscoelastic properties and stress-strain behavior). The relationship of the dynamic properties of hydroxyl terminated acrylonitrile-butadiene copolymer-methacrylate IPNs with the ratio of two components and the side group in methacrylate polymers were studied by torsional pendulum analysis (128). The IPN could be compatible depending on the side group in methacrylate polymers. The peaks in mechanical damping vs. temperature plots of IPN containing poly(Bu-methacrylate) and poly(iso-Bu-methacrylate) were broader than that of IPN containing PMMA.

2.2.4 **Other Important IPN systems Involving Polyacrylate or Copolymer of Acrylate or Modified Acrylate as one of the Components**

Klemm et al. studied polymer alloys containing spiro ortho
esters and methacrylate, prepared by simultaneous polymerisation (129). The system gave glassy, hard semi IPN with a milky non-transparent appearance.

Hoerhold et al prepared transparent impact resistant polymethyl methacrylate IPN with polyester - polyethers having low volume shrinkage by simultaneous thermal or photochemical polymerisation of MMA (I), ethylene glycol dimethacrylate (II) and 2 phenoxyethyl - 1,4,6-trioxaspiro (4,4) nonane (III) or III and 2,2-bis-(1,4,6 trioxaspiro (4,4) nonane-2 methoxy phenyl)propane (IV) in the presence of Bz$_2$O$_2$ and Et$_3$O$^+$SbCl$_6^-$ as initiators (130). Thus, a mixture of I 9.0, II 1.0, III 9.0, IV 1.0, Et$_3$O$^+$SbCl$_6^-$ 0.1, and Bz$_2$O$_2$ 0.5 g was homogenized and polymerised 8 hours at 80°C to give a transparent, impact resistant, insoluble (inorganic solvent) polymethacrylate - polyester - polyether IPN having density 1.214 g/c.c.

Simultaneous interpenetrating network polymers which are transparent, O$_2$-permeable, flexible, biocompatible and resistant to hydrolysis and biological degradation, useful in contact lenses, are prepared (131) by polymerisation or hydrophilic(meth)acrylic acid esters or amides and/or N-vinylpyrrolidone with crosslinking agents in the presence of crosslinking siloxanes. The film obtained from the published recipe was flexible without immersion in H$_2$O.

The amount of grafting monomer (glycidyl methacrylate (I)) profoundly affected the morphology and mechanical behavior of simultaneous interpenetrating networks of phthalic anhydride -
crosslinked epon 828 with crosslinked Bu-acrylate - diethylene glycol dimethacrylate copolymer (132). Electron microscopy, dynamic mechanical spectroscopy, and Gehman torsion experiments showed that the compatibility of the epoxy phase and acrylate phase increased with grafting and at the point of compatibility between the two networks, the supermolecular structure could be visualized as becoming one complex network, when the number of grafts between the two polymer chains outnumbered the number of homopolymer crosslinks. It was stated that the chemical graft significantly altered the free energy of mixing of the two polymers, and at well defined levels of grafting, the free energy of mixing went from positive value to a negative value.

2.3 Interpenetrating Polymer Networks based on Polyacrylates and Polystyrene

Systems under this heading have been covered by many authors. A considerable number of publications can be found on this particular system. Here, in the present thesis, only a concise review is presented.

2.3.1 IPN systems based on Poly(Bu-acrylate) and Polystyrene

This is probably the most important area under the IPN systems based on polyacrylate and polystyrene. The elastomeric properties of poly(Bu-acrylate) is applied to modify and improve the toughness properties of rigid, brittle polystyrene.

The general physical and mechanical behavior of the interpenetrating networks and semi-I IPNs (polymer I crosslinked only)
of poly(Bu-acrylate) (I) and polystyrene (II) appeared similar, except that in the glass-rubber transition region, the two T_g's are more pronounced for the semi-I IPN, indicating greater molecular separation (133). A series of poly(Bu-acrylate)/polystyrene IPNs and semi-I IPNs with deliberately controlled graft levels, were synthesized via an urethane chemical coupling method. A series of semi-II IPNs were also prepared with the molecular weight of a crosslinked polymer (A) as variable. The more highly grafted IPNs displayed poorly defined morphologies in which the domain structures were irregular and phase domain boundaries were characterised by fibrillar and interphase regions. Single phase transition peak was another feature of the more highly grafted IPNs. Polymer A network formed in the presence of a linear polymer (B) results in morphologies dependent on the molecular weight of linear polymers. In the semi-II IPNs, polymer A, molecular weight below M_v = 20,000, caused polymer B to behave like a plasticiser or a diluent. The domain size of semi-II IPNs agree well with theoretical predictions developed by the authors (134). Poly(Bu-acrylate) - polystyrene sequential IPNs of various compositions were made by UV photopolymerisation by Widmair et al. (135). Poly(Bu-acrylate) served as network A and polystyrene as network B. Acrylic anhydride (I) and divinylbenzene were used as labile and permanent crosslinker respectively. Two series of IPNs were prepared depending upon which network contained the crosslinkers. After IPN formation the I containing network was decrosslinked and solvent extracted.
The critical experiments had the I in network A. After extraction of network A the density of the remaining network B was 0.7-0.9 g/c.c. SEM of network B revealed a porous but continuous structure formed by aggregate of fused spherical polystyrene domains. Shear modulus temperature curves and Shear modulus composition curves at room temperature and at 160°C (rubbery modulus) were obtained for Bu-acrylate-tetraethylene glycol dimethacrylate copolymer IPN and semi IPN with divinyl benzene styrene copolymer and compared with those of series of Bu-acrylate - divinyl benzene tetraethylene glycol dimethacrylate styrene copolymers (random copolymers). The data including morphology and phase inversion were discussed in terms of various mechanical models (136). 

Sperling et al made a comparative study on semi-II IPNs and full IPNs. Sequential poly(n-butyl acrylate) (I) and polystyrene (II) semi-II and full IPNs of various composition were made by UV photopolymerisation. Acrylic anhydride and divinyl benzene were used as labile and permanent crosslinkers respectively for the rubbery and plastic phases. After IPN formation I was selectively decrosslinked. After extraction of I the remaining II network was characterised by swelling measurements and examined by SEM. Crosslinked I affect the formation of second network more than does uncrosslinked I. A porous phase formed by an aggregate of spherical II domains was observed. The experimental domain diameter was found to be in good agreement with theoretical values. A significant level of molecular mixing was found for full IPNs of midrange composition. With the destruction of crosslink sites, there is no
longer a forced miscibility of the interlocked phases, which are thermodynamically incompatible (137). Yeo and coworkers studied a series of sequential IPNs comprising of poly(Bu acrylate) and polystyrene, and an equation for predicting the domain diameters was found to be in good agreement with morphologies obtained by electron microscopy (138,139). The shear modulus was studied as a function of composition at 25°C. A series of new theoretical equations were derived for predicting the domain size in IPNs and related materials. The equations are based on a domain formation process comprising the crosslink density of each polymer, mixing and demixing thermodynamics, network swelling and elastic deformation of each polymer network, and the interfacial tension between two polymers. The new equations are applicable to both crosslinked and linear materials. The theory was applied to poly(Bu-acrylate)/polystyrene IPNs and semi IPNs. Widmaier et al studied the nature and extent of dual phase continuity in sequential IPN via scanning electron microscopy. Polystyrene (I) - poly(Bu-acrylate) (II) IPN cross-linked with divinyl-benzene (III) and acrylic acid anhydride (IV) respectively, were decrosslinked by hydrolysis with NH₄OH and extracted to determine their dual phase continuity. Hydrolyzed IV crosslinked rubber II was extracted from the interpenetrating network to leave the III crosslinked plastic I as a homopolymer network with a connected sphere morphology. The extracted network was also continuous in space. Interpenetrating networks of crosslinked poly(Bu-acrylate) and crosslinked polystyrene have both phases continuous provided that sufficient
amounts of both polymers are present. The completeness of extraction showed that little grafting occurred (140, 141).

Ionomer/ionomer thermoplastic IPNs based on poly(Bu-acrylate) and polystyrene was studied by Sperling and coworkers (142). The chemically blended IPNs had higher melt viscosities than the compositionally equivalent mechanically blended IPN. Dual phase continuity was suggested for the chemically blended IPN. Two glass transitions were observed for both the IPN. The chemically blended IPN composition and higher tensile strength and average elongation than the mechanically blended IPN.

Sperling et al. described a thermodynamic model for predicting the domain size in IPN (143). The experimental variables required to determine the domain size include the volume fraction and crosslink density of each polymer, the interfacial tension and the temperature. The predicted domain sizes agree with those observed by electron microscopy of IPN prepared by copolymerizing divinylbenzene and styrene in swollen copolymers of Bu-acrylate and acrylic anhydride. Interpenetrating networks of Bu-acrylate-tetramethylene dimethacrylate copolymer (I) divinyl benzene styrene copolymer or semi interpenetrating network of I with polystyrene were studied for glass transition by dynamic mechanical spectroscopy and for morphology by electron microscopy as a function of composition and crosslink density (144). Transition broadening and single intermediate broad glass transition peaks were observed at low or high crosslink density. At low crosslink density and intermediate composition ratio, the morphology was a cellular domain structure while at higher crosslink density the domains were of irregular
2.3.2 Poly(Bu-methacrylate)-Polystyrene Interpenetrating Polymer Networks

The effect of the formation – kinetics of a semi IPN on microphase separation or vice versa was investigated in systems prepared by copolymerising styrene with divinyl benzene in the presence of various amounts of poly(Bu-methacrylate) at different temperatures (145,146). The formation of semi IPN proceeds under non-equilibrium conditions. Depending on the reaction rate and the rate with which the viscosity increases, the thermodynamic incompatibility and microphase separation begins at different conversion stages. Thus the kinetics of semi IPN formation determines the beginning and affects the phase separation. The reaction do not change at conversion corresponding to the beginning of the microphase separation. The latter in semi IPN follows the spinodal mechanism and therefore does not affect the reaction kinetics. Phase separation of semi IPN formation was also investigated by light scattering. The time for phase separation was measured as a function of the rate of the copolymerisation reaction and of the composition of the initial blend. The time until the beginning of phase separation decreased with increasing content of poly(Bu-methacrylate) in the blend. The change in concentration of divinylbenzene did not influence the process of phase separation.

Optical scattering at 441.6 nm from a He-Cd laser was used to study microphase decomposition in the formation of pseudo-interpenetrating networks (PIN) based on poly(Bu-
methacrylate) (I) and crosslinked styrene-divinylbenzene copolymer (147). Plots are presented of the scattered light intensity Vs time for PIN containing 10 and 20% I at 333 and 343 K. The mutual diffusion coefficients and dimensions of heterogeneous microregions are given as function of temperature and I content. The microphase decomposition is governed by a complex spinodal-nucleation - growth mechanism. The initial stages of phase separation in formation of semi IPNs based on a divinylbenzene - styrene copolymer and poly(Bu-methacrylate) were studied by Lipatov et al. using an optical laser diffractometer (148). The phase separation obeyed the mechanism of spinodal decomposition.

2.3.3 Other Important IPN Systems based on Polyacrylate and Polystyrene

Effect of decrosslinking and annealing on Interpenetrating polymer networks prepared from poly(ethyl acrylate)/polystyrene combination was studied by Neubauer et al. (149). The effect was studied by systematic decrosslinking and annealing on interpenetrating polymer networks of polystyrene and poly(Et. acrylate) crosslinked by various amounts of acrylic anhydride which was hydrolyzed by soaking 24-28 hours in an NH₃-water mixture. On annealing, the phase continuity of the polystyrene component was increased relative to the poly(Et. acrylate) component and separation of the phases was more pronounced. For totally decrosslinked samples, a chemically induced blend with an unique morphology was obtained.
Kolarz et al studied the properties and structure of IPNs composed of divinyl benzene-styrene copolymer (I) and divinyl benzene - methacrylic copolymer Na salt (II). The properties of the hydrophilic II network outweigh those of the hydrophobic I network. The sorption properties of these systems toward large organic ions are much better than those of ion exchange sorbents obtained only from II. Kolarz, et al also reviewed the method for studying IPN, and results are presented from the investigation of the structure of the IPN system having divinylbenzene methacrylic acid copolymer (I) and divinylbenzene styrene copolymer (II) by determination of its swelling capability in selected solvents and in water (150,151).

Hourston et al. studied IPN systems involving Acronal - poly(methyl-acrylate) (152). In this study, crosslinked Bu-acrylate - styrene copolymer (Acronal 230D) was swollen with Me-acrylate and divinylbenzene which were polymerised in situ giving interpenetrating networks containing 70,50,35 and 25% divinyl benzene - methacrylate copolymer (I). Electron microscopy showed that interpenetrating networks to be two phase materials with I domain size increasing with I content. Longitudinal Sonic velocity measurement shows that both phases become continuous at 50% I content whereas dynamic mechanical spectroscopy shows that the constituent networks are not extensively mixed.