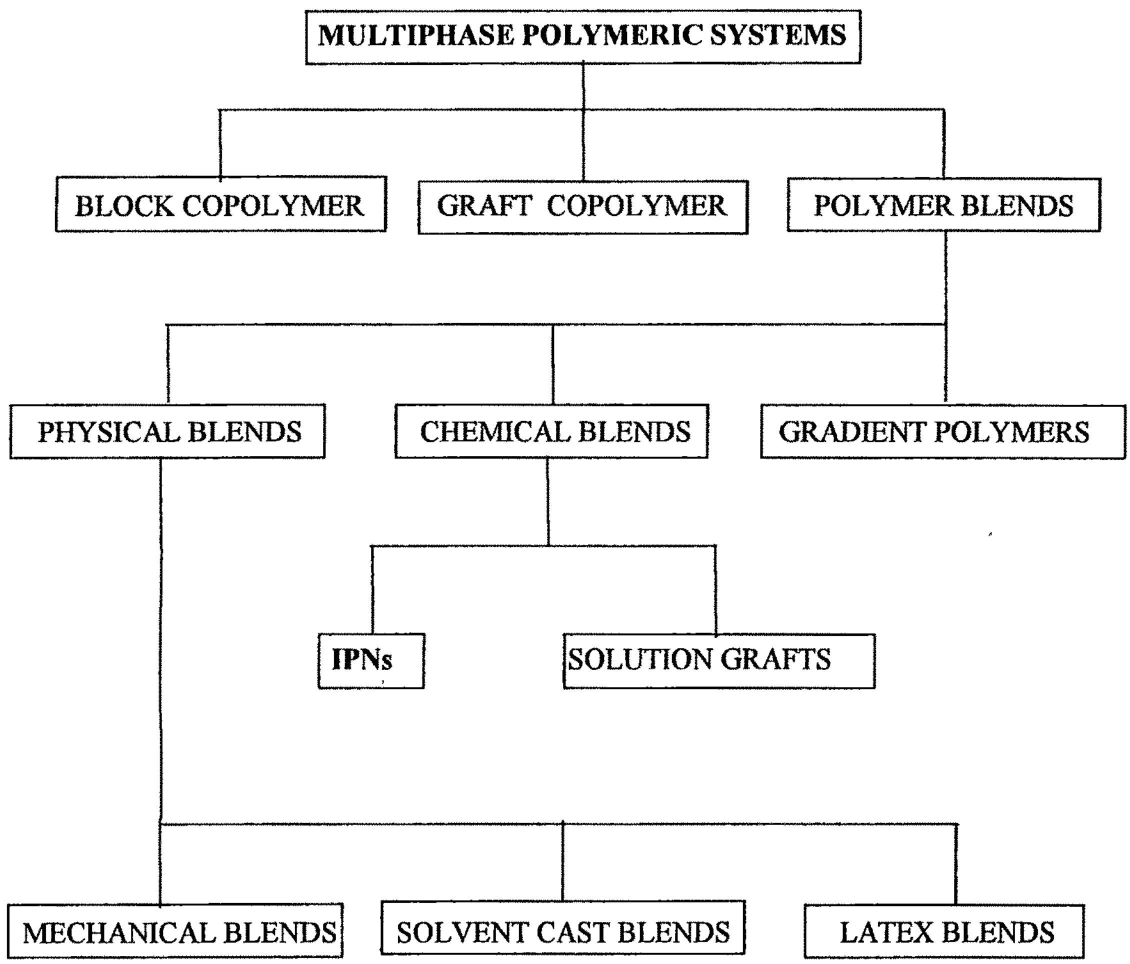
Chapter I

GENERAL INTRODUCTION

Polymers have become the most versatile commodity in today's life style of the mankind Due to global competition, there is an ever growing demand for improved product properties and quality at economic price. As a result, it has become necessary to develop polymer materials of tailor made properties either through new invention or through the modification of existing polymers This has lead to widespread interest in multiphase polymeric systems[1-3]

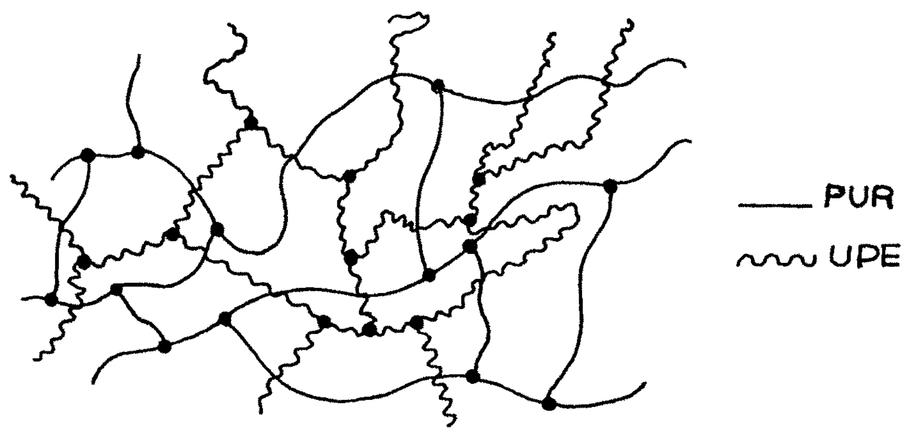
Multiphase polymeric systems are classified according to the group theory concept of Sperling[4] as shown below



Out of the many types of multiphase polymers, physically blended polymers can be most easily prepared However, it results in a coarse multiphase morphology due to thermodynamic incompatibility of the components The entropy of mixing of two polymeric species is very small as very long chains are involved Coupled with the usually positive heat of mixing, the resulting free energy of mixing is positive, causing these materials to undergo phase separation Due to the lack of chemical bonding between the two phases, many polymer blends may experience serious phase distortion problem during the processing stage or phase migration problem after a period of service time

Graft and block copolymers are considered to be better than the physically blended polymers in the sense that chemical bonding between the two phases may enhance the interface stability of these multiphase polymers. However, commercial graft or block copolymers are mainly limited only to thermoplastic polymers

Interpenetrating Polymer Networks (IPNs) are different from those mentioned above. They are novel type of polyblends consisting of two or more crosslinked polymer networks held together by permanent interlocking of entangled chains with only accidental covalent bonds between the polymers. This is the only method for intimately combining two crosslinked polymers, the resulting mixture exhibiting only limited phase separation. A general schematic representation of a two component IPN is given below



Interpenetrating Polymer Networks are referred to as catenanes[5-7] and are the youngest in the field of polymer blends and have got two major characteristics compared to other systems

1 The enhanced degree of intermixing between the component polymers due to restricted phase separation caused by interlocking of networks, which can play a significant role in enhancing the interfacial adhesion in phase separated materials

2 The possibility of morphology control by varying the kinetic parameters, which enables the synthesis of IPNs with dispersed phase domains ranging from a few micrometer to a few tens of nanometres and finally to those with no resolvable domain structures[8]

Since there are two components in an IPN, the synthesis of IPN can be classified according to the polymerization sequence and the polymer structure There are two types of IPNs according to the polymer sequence They are,

1. Simultaneous IPN
2. Sequential IPN

In the first case, both the monomers/prepolymers are introduced together along with the initiator and crosslinker, and polymerized in situ Ideally, both monomers are reacted simultaneously but independently In a simultaneous IPN, ideally, the chains of neither polymer should be perturbed or extended By varying the reaction scheme, many materials may be made that do not fit clearly into one category or the other

The sequential IPN begins with the synthesis of a crosslinked polymer 1 The second monomer along with its crosslinker and initiator, are swollen into polymer 1, and polymerized in situ Thus sequential IPN is a material in which network 1 is fully formed before monomer 2 is introduced Thus, the chains are extended by the swelling action of monomer 2, and the phase domain size is greatly reduced

According to polymer structure, IPNs are classified into two types

1. Full IPN
2. Semi IPN (Pseudo IPN)

A full IPN is formed when both the components are crosslinked When only one of the polymers is crosslinked, the product is termed a semi-IPN. For a given system, two different semi IPN exist When the first formed material, polymer 1, is crosslinked, a semi- 1-IPN results If however, polymer 1 is linear and polymer 2 is a network, the material resulted is known as a semi-2-IPN

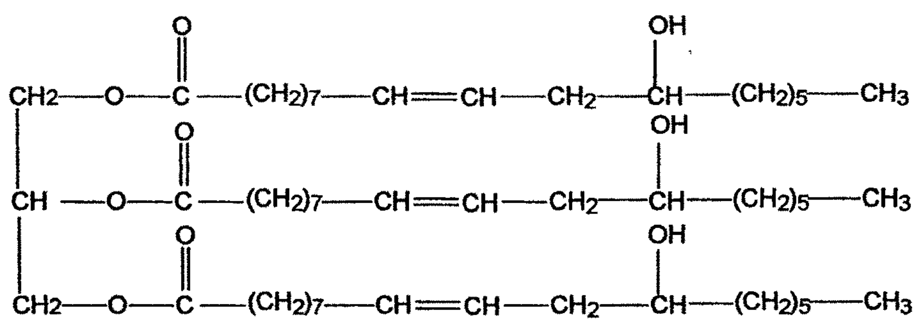
Another class of IPN is the Interpenetrating elastomeric network The synthesis takes two latexes of linear polymers, mixes and coagulates them and crosslinks both components simultaneously

RENEWABLE RESOURCES

Concern for the stability of future petroleum supply has stimulated much attention in the past few years towards the need to emphasis natural renewable materials as replacements or substitutes for product materials now derived from petroleum and coal However, going beyond the set idea of replacement or substitute materials, renewable resources have valuable, sometimes different properties of their own

The term "renewable resource" has come to mean sources of energy or products that can be used, grown or replenished naturally, time after time, as opposed to mineral and petroleum products which once depleted are gone for ever Among the various renewable resources available, plant products rank very high viz wood, cellulose, starch, rubber and triglyceride oils.

Many plants yield valuable oils, such as corn oil, linseed oil and cottonseed oil Besides food uses, these oils provide the basis for paints, adhesives and other industrial uses due to the presence of multiple double bonds, which allow the ready polymerization of these oils. Agro based renewable resource like castor oil (CO) is unique among vegetable oils due to the presence of another reactive site like hydroxyl group in addition to points of unsaturation The number of hydroxyl groups and double bonds are identical in castor oil, at three each per molecule The structure of castor oil is as follows



Because of their high reactivity, they offer special industrial advantages, allowing the synthesis of products like polyesters and polyurethanes. Later on research has slowly shifted to other areas including

IPNs based on elastomers from various botanical oils coupled with other vinyl polymers which resulted in a series of tough plastics of reinforced elastomers, depending on the relative quantities of each product

POLYURETHANE/ACRYLATE IPNs

Because of their high transparency, certain polymers like acrylates have been utilized for many years for optical purposes, although they do not meet all the other requirements e.g. good scratch or impact resistance. Thus, the introduction of an elastomeric phase on to acrylates yield materials with improved properties.

Interpenetrating and semi interpenetrating polymer networks based on polyurethanes (PUR) and polyacrylates is the subject of great interest among researchers However this method is not valid when transparency is required, as the mixing of two polymers usually yield opaque materials except when the components have nearly the same refractive indices Various acrylates like methyl methacrylate (MMA),butyl acrylate (BA), Hydroxy ethyl methacrylate (HEMA), methyl acrylate (MA) and various copolymers of acrylates with other vinyl monomers like styrene are employed in the preparation of IPNs with polyurethanes.

Sperling and other researchers[9-15] started work on acrylate based sequential IPNs in the early 70's The first latex IPN (LIPN) reported by Frisch et al[16] in 1969 was based on a PUR and polyacrylate latices. Simultaneous IPNs were also reported first by Frisch[17] by mixing a urethane prepolymer with a low molecular weight epoxy resin

A series of three component IPNs based on polyurethanes and various acrylates have been reported by different authors[18,19] The glass transition studies showed three separate but broad Tg's corresponding to each component. The mechanical loss and tensile strength of mica filled IPNs based on Dimethyl amino ethylmethacrylate have been reported by Wang et al[20]. The results are compared with the unfilled one

The properties of the IPNs depend very much on the synthetic conditions like temperature, pressure, catalyst etc. IPNs synthesized at high pressure of the order of 20,000 kg/cm^2, showed a very broad glass transition ranging from (0-100)°C[21] Hourston et al[22] have reported PUR/Poly(methylacrylate) IPNs synthesized at 200 MPa and at a range of temperatures The mechanical properties of IPNs synthesized under more standard conditions have been reported by Morin et al[23] Decreased synthetic temperature generally result in improved mixing of the two networks whereas high synthetic temperature is found to affect the mechanical properties of the material adversely

Photopolymerization[24] and radiation initiated polymerization[25,26] were found to be effective in obtaining networks with a high degree of interpenetration It was found that the extent of component mixing and the size scale of heterogeneties can be reduced by including radiation exposure during the synthesis The volumetric dilatometry study of a gradient IPN[27] showed that, the temperature transitions, composition and microphase separation are different at different depths inside the sample.

The mechanical properties and morphologies of various semi-IPNs have been reported by many researchers[28-31] The mechanical, dynamic mechanical behavior and density of semi-1 IPN , semi-2 IPN and grafted IPNs[32-34] based on PUR-polyacrylate have been reported by Hourston and coworkers In a recent study[35] a nonlinear optical polymer based on PUR/PMMA was prepared in which PMMA was treated with a disperse red 19 dye and interpenetrated with PUR.

Polyurethane based IPNs are known for their damping and energy absorption characteristics The damping behavior of PUR/acrylate based IPNs were found to vary with catalyst concentration and component composition[36-37] The fatigue crack growth and the fracture toughness were also found to increase with the PUR content in such IPNs

Other interesting areas of research in this class are, IPN based adhesives[38,39], binders[40] and coatings[41,42] Dang Huiti[38] reported an adhesive based on PMMA in which the second component, PUR was based on a renewable resource, castor oil The adhesive property was found to vary with the composition of components and NCO/OH ratio in all the cases.

Reaction Injection Molding (RIM) and Reinforced Reaction Injection Molding (RRIM) materials are based on polyurethane technology, due to the high reactivity of OH groups with NCO groups. Castor oil has been extensively used in RIM, RRIM[43-46] and high pressure impingement mixing[47]

It is of utmost importance to establish the kinetics of IPN formation as the properties of the resulting material depend upon the nature of all the reactions and side reactions taking place during their synthesis Various techniques like FTIR, DSC, microdilatometry, reflectance spectroscopy etc have been employed by various researchers to establish the kinetic aspects of IPN formation[48-55] The kinetics of boundary layer formation of PUR/Polyester acrylate system has been reported by a Russian author[50] by using an attenuated total reflection IR spectroscopy In a recent report[56], changes in functional group concentration were monitored by FTIR during the synthesis of an IPN at different temperatures and it was found that IPNs possess a lower rate constant and a higher activation energy than the respective homopolymer networks

The morphology and hence the properties of various IPNs based on polyurethane and acrylates have been reported[57-64]. The effect of composition, chain grafting agent and the chain structure of soft segment on the properties have been explained Dynamic mechanical analysis (DMA) and transmission electron microscopy/scanning electron microscopy have been extensively used to study the phase morphology and extent of mixing of the component network[55,65-69]. Depending on the morphology, a single tan δ, broad tan δ or even two distinct tan δ peaks were observed

There are numerous reports on PUR/acrylate IPNs, where the PUR is based on a renewable resource, castor oil[70-72] The low molecular weight oligomers resulted from CO by reacting it with various diisocyanates have been interpenetrated with various acrylates for the synthesis of IPNs Suthar and coworkers have studied the various properties of CO based IPNs with various acrylates like PMMA[73-76], PMA[61,77], PEA[78,79], PEMA[80-81] and so on The DMA and solid state NMR studies of castor oil based IPNs have also been reported by various authors[24,60,65] The kinetic studies showed that the rate of formation of PUR is faster than the acrylates in the case of CO PUR/acrylate based IPNs[54,63,82,83] The gelation time of IPNs is found to decrease with increase in PUR content.

POLYURETHANE/POLYSTYRENE IPNs

Polystyrene (PS)is another plastic material which is used considerably to prepare IPNs by combining it with polyurethanes IPNs and semi IPNs based on PUR/PS are being investigated in many laboratories round the world[84-88]. Various techniques like Small Angle X-ray Scattering (SAXS), Diffraction method and Differential Scanning Calorimetry (DSC) have been used to characterize these materials[89-92]. It appears that the parameters like, the crosslink density of both the networks and inter network grafting at various levels have a marked influence on the final properties of these materials

Ionomeric PUR/PS IPNs containing mutually opposite charge groups have been reported by Hsieh and coworkers[93-95] The effect of compositional variation, presence of solvent and reaction temperature on the properties of IPNs have been reported by many authors[96-98] The enrichment of PUR phase on the surface of the IPN was revealed by SEM, FTIR, ESCA and contact angle measurements In a recent report[99], it was showed that the compatibility between the components improved when dibutyltin dilaurate (DBTDL) was used as the catalyst for the PUR phase

Various techniques like IR, FTIR, Torsional braid analysis and Optical microscopy have been employed to study the kinetics of formation of PUR/PS IPNs[100-102] The thermodynamics of phase separation have also been examined by the authors

Castor oil based PUR have also been employed by many researchers[103-106] in the preparation of IPNs with polystyrene The properties were investigated as a function of the weight composition of the components and amount of crosslinking agent Cross polymerization / magic-angle-spinning ^{13}CNMR were used to study the microphase structure and structure-property relationship by Hsuing and coworkers[107] The size of the micro phase structure was found to be ~ 100 A

POLYURETHANE/EPOXY IPNs

The combination of PUR with plastic epoxy were found to produce a rapidly reacting simultaneous IPN The high viscosities and abrasiveness of the filled system like RRIM materials can be overcome by the use of simultaneous IPN based RIM systems involving PUR and epoxy resin[108-109]

Advanced IPN damping materials for marine applications have been prepared from PUR and epoxy polymers[110-112] Higher miscibility and increased density were observed for IPNs containing low molecular weight polyols The DMA analysis of a PUR/Bisphenol A epoxy resin IPN[113] showed that the PUR introduced can be incorporated in either the α or β transition domain of the epoxy

Castor oil based PUR were also used to prepare IPNs with epoxy resins. The amount of cross linking agent, DMP 30 required for the IPN was determined theoretically by Ma Song[114], and the results agreed well with the experimental data The stress - strain properties and dynamic mechanical behavior of these IPNs were studied in detail by many authors[115-117]

PUR/epoxy IPNs were found to act as better coatings for high temperature applications[118,119]. They also showed good corrosion resistance Yuwei and coworkers[120] have studied the effect of type of polyols, crosslinking catalysts and inorganic fillers on the DMA and mechanical properties of IPN damping coatings

In a recent report, Lian and coworkers[121] have monitored the kinetics of formation of a PUR-vinylester epoxy resin IPN using an online FTIR connected to a portable mini RIM machine The PUR formation in the IPN was found to be slow compared to that of pure PUR formation

MISCELLANEOUS IPNs BASED ON POLYURETHANE

Apart from general glassy materials which are used to a greater extent like acrylates, styrene and epoxy, many other polymers are also used for preparing IPNs with polyurethanes

FTIR, DSC and SEM have been used to study the kinetics of formation and the micro phase separation of various IPNs of PUR with phenolic resins[122], vinyl ester[123-126] and furan[127] A 2-HEMA terminated PUR/PUR IPN membranes were prepared by Liu et al[128] Small angle neutron scattering has been used as a tool to study the degree of micro phase separation in a Poly (carbon-urethane) and Poly (vinyl pyridine) IPN[129]. The domain size was found to be 100 A in the samples with one glass transition, and was found to be more in samples with two transition temperatures

The flexibility of nitrocellulose coatings for leather was improved by interpenetrating it with castor oil based PUR (COPUR)[130-131] Enhanced miscibility of the components was observed by the partial replacement of cellulose nitrate with vinyl chloride-vinyl acetate copolymer The adhesive behavior of COPUR/Poly (chloroprene) rubber IPNs have also been studied by peel and tear strength measurements[132] Adhesive strength of IPNs were found to be affected by the presence of solvents and acids[133]

POLYURETHANE/POLYESTER IPNs

Polyester is another glassy polymer having good thermal stability but low elongation and poor impact strength By combining it with polyurethane, a good elastomer, materials having better properties can be prepared Many reports have come up already in this area, where the polyester (PE) used is generally an unsaturated one (UPE) A vinyl monomer like styrene is used as the crosslinker for the polyester phase and an isocyanate for the polyurethane phase

Several two component IPNs based on a PUR and a commercial grade PE have been reported by Meyer[134] and Frisch[135] Many of these were developed for slow processes like casting and coating and showed enhanced mechanical properties. For fast processes such as in RIM applications, there are a few commercially available IPN compounds based on PUR and PE developed by different companies[136]. The processing conditions such as molding pressure, temperature, compound composition and reaction rate can all affect the morphology and the physical properties of these IPNs[137-144] The formation of urethane and unsaturated polyester in one material results in hybrids, which often have properties superior to either of the constituent polymers An added advantage of these hybrid systems is that, the heat generated by the mixing activated polyurethanes can internally trigger the thermally activated free radical polymerization of the unsaturated polyester resin

The reaction kinetics[137], crystallinity[145] and structure-property processing relationship[146,147] using DMA and electron microscopy have been studied by many authors. Results showed that the interaction between the two polymerizations and the reaction profile depend strongly on the compound composition, reaction sequence, type of catalyst and crosslinking nature of the constituent polymers[137] Results also revealed that the PUR reaction in the IPN resembles a solution polymerization before gelation and a bulk polymerization after gelation[142]

Chou and coworkers evaluated the morphology - kinetic-rheology relationship and mechanical behavior of various types of PUR/PE IPNs[148-150] by Light scattering and DMA studies It was found that, weight composition of the components and processing conditions play a major role in the phase separation behavior[151-154]. Lee and coworkers[145,146,155] have reported that the viscosity rise during the synthesis of PUR/PE IPNs could be due to the grafting reaction between the hydroxyl or carboxyl end groups of PE with isocyanates They have used a Rheometric dynamic analyzer in the oscillating mode to follow the rheological changes and gelation at isothermal conditions They found that when dibutyltin dilaurate was used as the catalyst for the PUR phase, the phase separation period from the onset of spinodal decomposition to gelation strongly affected the final morphology of the IPNs[145].

The effect of hard segment content on a PUR/PE elastomer on their solution properties was studied and compared with the phase separation state by Hetrich et al[156]. Hsu Chi Fan[157] has studied the interphase reaction in the catalysis of these IPNs Recently, H Xiao[158] of Detroit University has developed an IPN containing UV curable coatings using urethane modified acrylic resins based on free radical and cationic crosslinking mechanisms

The thermal properties, mechanical properties, reaction kinetics and morphology of PUR/PE hybrid networks were reported by various researchers[159-162] In a recent report[163], atomic force microscopy have been employed to study the phase separated surface of a PUR/UPE IPN It was found that the PUR moieties were preferentially dispersed on the surface of UPE matrix in the form of clumps or circular plates with sizes ranging from nanometers to micrometers

SCOPE OF THE PRESENT INVESTIGATION

Unsaturated polyester (UPE) resins are the most versatile resins, because of the low cost and wide range of compositions and compounding possibilities They have found applications in various avenues like automotive and lining industries They have good adhesive property to different types of substrates and reinforcements, and possess superior electrical properties along with good thermal stability UPE resins with such excellent properties are relatively rigid which may cause craze/crack growth and subsequently failure when subjected to the application of impact blows or stresses. This can be improved by toughening them through incorporation of judicious quantities of elastomeric materials like rubbery acrylates, polysiloxanes and polyurethanes.

Among the various elastomeric materials, PUR have proven to be the most versatile, as they can be tailor made having a wide range of physical properties from flexible foams to tough elastomers and to long wearing coatings They impart toughness but lack in thermal stability at higher temperatures[144] Thus interpenetration of rigid UPE and elastomeric PUR is expected to result IPNs of superior permanence in physical properties than their counterparts. The use of interpenetrating network formation offers potentially improved behavior because, the interpenetration gives good adhesion between the partially phase separated domains by physical interlocking of networks

A considerable amount of work has been reported in IPNs based on UPE and PUR networks Literature reveals that polyols used in the synthesis of PUR and IPN formation with UPE are mainly petrochemical based Efforts have been made during the past few years to replace expensive non-renewable polyols with low cost renewable materials in the production of PUR Among agro based renewable resource, castor oil stands out, as it has low cost and amenability to chemical reactions due to the presence of hydroxyl groups However, the reports on the synthesis of IPNs from castor oil based polyurethanes and UPE are very few Thus the main objective of the present work is to develop castor oil based IPNs having wide range of properties by simultaneously interpenetrating two polymers viz UPE and PUR based on castor oil differing in their chemistry.

The present study includes the synthesis of IPNs based on polyurethane and unsaturated polyester and their characterization by mechanical, thermal, dynamic mechanical and scanning electron microscopy The molecular weight between two crosslinks were determined by swelling method The sorption behavior of the IPNs were also studied in various solvents

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