

APPLICATIONS OF WATER SOLUBLE POLYMER BLENDS

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ABSTRACT

Polymer science is one of the most active and promising branches of science covering a multitude of topics from natural polymers to synthetic high polymers. The tremendous development in this area was responsible for the production of synthetic films, fibres, elastomers, plastics, nano-polymers, inorganic polymers, etc. Polymers have replaced metals and wood in light weight structural materials in automotive parts, electronic goods, and building materials and breakthroughs in contemporary medicine and surgery were possible only through the availability of man-made polymers. Some polymers are obtained from natural resources and then chemically modified for various applications, while others are chemically synthesized and used. Water soluble polymers due to their blood compatibility, non-toxic, non-immunogenic, non-mutagenic and non-carcinogenic nature finds applications in pharmaceutical, cosmetic, food, agricultural, and biomedical fields. In the present paper, the applications of only water soluble polymers and their blends are described.

Keywords: *Guar Gum, Miscibility, Polymer blends, Water soluble polymers, Xanthan Gum.*

I. INTRODUCTION

Polymer science is one of the most active and promising branches of science covering a multitude of topics from natural polymers to synthetic high polymers. There is no product so widely used in every sphere of life like polymeric materials designated as resins, resinous materials, plastics and elastomers. They were found to have many physico-chemical properties different from those of common low molecular weight compounds. With the establishment of the fact that the polymers are constituted of macromolecules, the chemistry of macromolecules advanced at rapid stride and the tremendous development in this area was responsible for the production of synthetic films, fibres, elastomers, plastics, nano-polymers, inorganic polymers, etc. Polymers have replaced metals and wood in light weight structural materials in automotive parts, electronic goods, and building materials and breakthroughs in contemporary medicine and surgery were possible only through the availability of man-made polymers.

Research works in Polymer Blends, Polymer Colloids, Polyelectrolytes, Electroluminescent Polymers, Thermoplastic Elastomers, Liquid Crystalline Polymers, Biomedical Polymers, Polymer Microgels, Polymer

Composites, Inter Penetrating Networks, Conducting Polymers, etc has introduced specialty polymers which have tremendous applications in all the fields of biomedical and engineering.

A literature survey has been done in the field of miscibility of polymer blends/water soluble polymers/applications of water soluble polymers/blends from Chemical Abstracts available in the library of Indian Institute of Science, Bangalore, India, in order to get a an idea about the different techniques already used and to have a comparative analysis. Till the end of the work the literature survey was continued wherever and whenever it was possible/necessary by utilizing the library facilities of Indian Institute of Science, Bangalore, India, University of Mysore, Mysore, India, National Institute of Technology, Mangalore, India, and Mangalore University, Mangalore, India. The authors also used the internet facility to collect research papers in this field of study. The following are some of the references relating to the field of research the authors came across during the survey.

II. WATER SOLUBLE POLYMERS

Water soluble polymers have a wide range of industrial applications like food, pharmaceuticals, paint, textiles, paper, constructions, adhesives, coatings, water treatment, etc. In this paper, the water soluble polymers have been divided into two categories: synthetic and natural. Some of the examples for synthetic water soluble polymers includes: Polyvinyl alcohol (PVA) [1], Polyacrylamides [2], Poly(ethylene glycol) (PEG) [3, 4], Polyvinyl pyrrolidone (PVP) [5-7], Polyacrylic acid (PAA) [8, 9], Polyphosphazenes [10, 11], N-(2-Hydroxypropyl) methacrylamide (HPMA) [12], Polyphosphates [13,14], Polyoxazoline [15, 16], and Divinyl Ether-Maleic Anhydride (DIVEMA) [17, 18]. Examples for natural water soluble polymers includes: Guar Gum [19-22], Xanthan Gum [23, 24], Pectins [25, 26], Starch or Starch Based Derivatives [27-32], Cellulose Ethers (Hydroxypropylmethyl cellulose (HPMC), Hydroxypropyl cellulose (HPC), Hydroxyethyl cellulose (HEC), Sodium carboxy methyl cellulose (Na-CMC)) [33-39], Chitosan Derivatives [40-45], Dextran [46-48], Albumin [49-51], and Carrageenan [52, 53].

III. POLYMER BLENDS

Now a days, polymers are playing an increasingly significant role in all branches of industry. Recent advances in science and technology are exploiting the versatile properties offered by new polymeric materials. With the advancement of civilization, man is always looking for a new material to meet the specific needs and challenges. The new materials should provide better properties and method of preparations should be available at affordable cost. In search of new polymeric materials, either new monomers are polymerized or copolymerization technique is used to get polymers with tailor-made properties. The extensive use of polymeric materials in technology and pharmaceutical application lead to the development of polymer blends.

Polymer blends, also known as polyblends are mixtures of structurally different homo-polymers, co-polymers or ter-polymers, which interact through secondary forces such as hydrogen bond, dipole-dipole forces, etc. and with no covalent bonding. Polymer blends have received much attention since blending is simple and effective approach to develop new materials, exhibiting combinations of properties that cannot be obtained by

individual polymers. The polymer blending may result in the reduction of basic cost, enhancement of performance and improved processability [54].

Blending is one of the most effective methods of manufacturing new polymeric materials. Blends can be produced that have properties independent of either the original homopolymers or structurally similar copolymerized macromolecules. However, mixing of polymers to produce novel materials is typically possible only if two compounds are miscible. It is important to relate the chemical structure of polymers to their physical properties, as miscibility is often a result of physical interaction between two materials. The advantage of combining polymers within a blend is twofold. First, as the blend is completely miscible, the physical properties of the material will be dependent not only on the constituent polymers but also on their interactions. As such, the material's key physical properties, such as its glass transition temperature and melting/decomposition regions, can be altered, depending on the molecular organization of the two polymers in the blend [55]. Second, the mixing of two polymers adds a second functionality with which the blend can form chemical or physical interactions. A polymer blend can act in similar manner to a mixed surfactant/polymer system, which can be used to enhance the interactions of incompatible compounds or bridge immiscible environments [56].

III. CLASSIFICATION OF POLYMER BLENDS

Based on the method of preparation, polymer blends are classified in to five groups as follows [57]: (i) Mechanical polymer blends, (ii) Mechano-chemical polymer blends, (iii) Chemical polymer blends, (iv) Latex polymer blends, and (v) Solution-cast polymer blends.

IV. POLYMER ALLOYS

Polymer alloys are a class of polymer blends in which a large interpenetration of domain is secured by either chemical or physical means. Blends are a direct result of the blending action and alloys are the final blends of well-defined morphology and have a set of properties. Utracki [57] clearly mentioned the interrelations in polymer blend nomenclature. These are presented in Fig. 1. From the figure, it is clearly evident that the immiscible polymer blends which are compatibilized results in a polymer alloy.

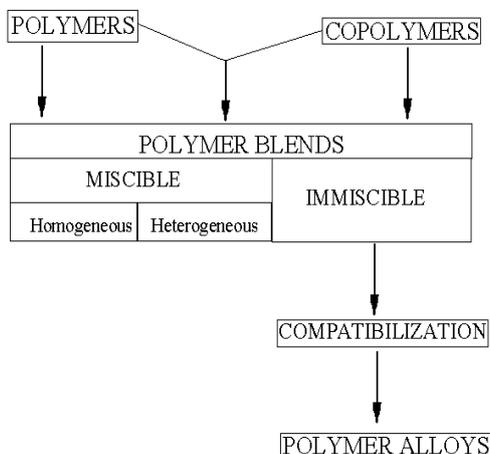


Figure 1: Interrelation in polymer blend nomenclature



V. MISCIBILITY OF POLYMER BLENDS

Polymer blends often exhibit properties that are superior to those of any one of the component polymers. However, the manifestation of superior properties depends upon the miscibility of polymers [58]. The term 'miscibility' refers to the formation of a homogeneous system at a molecular level. Depending upon the degree of molecular mixing the blends may be categorized as miscible polymer blends, semi-miscible polymer blends and immiscible polymer blends.

The state of immiscibility of a polymer blend does not preclude its utility, multiphase polymer blends also have made respectable inroads into the polymer market. Because of their specific advantages, multiphase polymer blends have extensive utility in applications requiring improved physical and mechanical properties. The best method of enhancing the miscibility of polymer blends is to introduce specific interactions. The potentially useful specific interactions are random dipole, induced dipole, dipole-dipole, ion-dipole, hydrogen bonding, acid-base and charge transfer interactions [57, 58].

VI. THERMODYNAMIC APPROACH TO MISCIBILITY OF POLYMER BLENDS

Polymer-polymer miscibility is determined by a delicate balance of enthalpic and entropic contributions to the free energy of mixing [59]. The change in free energy (ΔG) of the mixing is given by the equation $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$ where ΔH is change in enthalpy, ΔS is change in entropy and T is the absolute temperature. The unique factor affecting the thermodynamics of polymer blends compared with other low molecular weight systems is the large molecular weights of both the components. For spontaneous mixing ΔG_{mix} must be negative so that $\Delta H_{\text{mix}} - T\Delta S_{\text{mix}} < 0$. This implies that exothermic mixtures ($\Delta H_{\text{mix}} < 0$) will mix spontaneously. Whereas, for endothermic mixtures, miscibility will occur at higher temperatures. Since usually the enthalpy of mixing (ΔH_{mix}) is positive or close to zero and very small entropy of mixing (ΔS_{mix}) associated with the polymer mixtures, free energy of mixing becomes positive. Hence, most polymer blends are immiscible in nature.

VII. FACTORS INFLUENCING MISCIBILITY OF POLYMER BLENDS

The most common interactions that are involved in blends and enhance miscibility are hydrogen bonding, charge transfer complexes, ionic and dipole interactions. All these contribute to the negative enthalpy of mixing. As a result, it may be possible to select two polymers having chemical moieties within or attached to the chain which have the proper complimentary dissimilarity to yield an exothermic heat of mixing, although it should be recognized that there will still be an endothermic contribution from the dispersive interaction or Van der Waal forces between the remaining parts of the structure that do not interact specifically [60]. There are two types of miscible polymer blends: (i) miscible polymer blends having weak or little interactions and (ii) miscible polymer blends having strong specific interactions [61]. However, in the literature [62, 63] there is confusion about the definitions of "weak interactions" and "strong interactions." Since it is well established from the thermodynamic point of view that miscible polymer blends have "negative" values of Flory-Huggins interaction parameter (χ), but some investigators treated miscible polymer blends with $|\chi| \leq 0.001$ are having "weak



interactions” and miscible polymer blends with $|\chi| \geq 0.01$ are having “strong interaction” [64]. However, such a definition is somewhat arbitrary. Further, χ may not be an appropriate parameter that can define whether a miscible polymer blend has weak or strong interactions. It is more appropriate to describe whether a miscible polymer blend has weak or strong interactions in terms of intermolecular forces. Table 1 gives a summary of bond energy and relative strength of different intermolecular forces. Miscible polymer blends with Van der Waals interaction have “weak interactions” and miscible polymer blends with other types of interactions have “strong interactions” [65].

Table 1: Bond energy and relative strength of different intermolecular forces

Type of interaction	Bond energy (kJ/mol)	Relative strength
Ionic attraction	850 – 1700	1000
Hydrogen bonding	50 – 170	100
Dipole-dipole interaction	2 – 8	10
Van der Waals interaction	≈ 1	1

The majority of the known polymeric mixtures are immiscible, however, many miscible polymer blends were prepared in the last three decades. The behaviour of polymers in the mixture does not necessarily be the same as that of the isolated polymers. Methods must be found to determine the function of each polymer in its new environment and to answer questions concerning the separation of the phase, the identification of the predominant phase, the character of dispersed phase, and the interaction between the polymers. It is also reported that materials with close solubility parameters are readily miscible with each other [66]. Most of the polymer blends are heterogeneous, but these blends appear homogeneous when suitable compatibilizers are added to them.

VIII. EXPERIMENTAL METHODS TO DETERMINE THE MISCIBILITY OF POLYMER BLENDS

There are many different experimental methods that can be used to investigate the miscibility of polymer blends [67-71], such as Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analysis (DMTA), dielectric measurement, cloud point measurement, Small-Angle Neutron Scattering (SANS), Scanning Electron Microscopy (SEM), Fourier Transform Infra Red Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), etc.

Singh et al. [62, 72] and Gupta et al. [73] made an ultrasonic and viscometric investigation to study the miscibility of polymers. Kulashreshtha [74] used viscometric technique for the determination of compatibility. Hani Younes and Daniel Cohn [75] have conducted DSC and IR studies on the morphology of polyethylene glycol/polylactic acid blends. Masson and Manlen [76] made a wide angle X-ray scattering (WAXS), FTIR, DSC, DMA and solid state magic-angle spinning (CP-MAS) NMR investigation on the cellulose and polyvinyl pyrrolidone blend and reported that the blend is miscible. Hourston and Schafer [77] studied the morphology, phase continuity, and mechanical properties of polyether urethane/polyethyl methacrylate. Hourstone et al. [77, 78] used modulated-DSC for the thermal characterization of multi component polymers and inter phases.



Chee [79] described a method for the study of polymer-polymer miscibility by viscometry. As per his method the polymer blend will be miscible if the interaction parameter $\mu \geq 0$ and immiscible if $\mu < 0$. Sun et al. [80] gave a new equation for the determination of interaction parameter of polymer blends in solution by viscometric method. As per their theory, the polymer blend is miscible when the interaction parameter $\alpha \geq 0$ and immiscible if $\alpha < 0$. They further stated that α gives more reliable information when compared to μ because long term interactions such as hydrodynamic attractions or repulsion terms are taken into account in the determination of the expression for μ . Corradini et al. [81] probed the miscibility of PVC/EVA hydrolyzed blends by viscometric, microscopic, and thermal analysis and reported that the blend is miscible. They further reported that all these methods gave identical results.

Mihir Sheth et al. [82] carried out DSC and DMA analysis on biodegradable polymer blends of PLA and PEG and concluded that the PLA/PEG blend ranges from miscible to partially miscible, depending on the concentration. Pingping [83] gave a new criterion of polymer –polymer miscibility detected by viscometry and further reported that the new criterion is reasonable and polymer –polymer miscibility could be determined by viscosity. Katime et al. [84] studied the behaviour of PMMA in the PVC/THF binary mixture by viscometry and laser light scattering. Their results showed that compatibility of this blend depends not only on the molar masses of the samples but also on the concentration of the PVC.

Varada Rajulu et al. [85, 86] made an ultrasonic, viscometric, refractometric, density investigation on PVC/PS, PVC/cellulose acetate and cellulose acetate/PMMA blend systems in which these blend combinations were incompatible in nature and PVC/PMMA in cyclohexanone was found to be compatible. C. K. Yeom et al. [87] characterized the sodium alginate (NaAlg) and PVA blend membranes in pervaporation separation by SEM. He et al. [88] developed methods of microscopic observation and macroscopic characterization for determining the co-phase contained in immiscible binary blends. Chen et al. [89] used viscometry method for the miscibility studies of PEO/PVAc blends. Chattopadhyay and Banerjee [90] used visible spectroscopy, polarizing microscope, and FTIR techniques to study the miscibility of polymer blends. Mohamed and Sabaa [91] studied the miscibility and the thermal degradation behaviour of PVC/Poly (vinyl butyral) blend using DSC, TGA and tensile testing methods and reported the blend to be miscible. Elberaich et al. [92] confirmed the miscible nature of PEO/PMMA blend by using optical microscopy and DSC techniques.

Homogeneous mixing at molecular level is a prerequisite for polymer miscibility. Blending of the polymers in solution ensures effective attainment of equilibrium between different polymer components in solution. This method employs dilute solution viscometry. A large number of investigations have been carried out on the miscibility of polymer blends using viscosity measurements corresponding to the ternary system (polymer1/polymer2/solvent) [67, 74, 93, 94].

Additional advantages of dilute solution viscometry is that no sophisticated equipment is necessary and the crystallinity or the morphological state of polymer blends do not affect the results, making the viscometric method more convenient and handy for characterizing polymer mixtures. Recently many simple and rapid solution techniques have been used for probing the miscibility of polymer blends in solution [85, 95-98]. These techniques include the measurement of refractive index, ultrasonic velocity and density of the polymer blends in solution.



IX. APPLICATIONS OF POLYMER BLENDS

The development of polymer blend/alloy system requires a sound scientific basis and offers opportunity for many interesting polymer mixtures for commercial exploitation. The key to blending is economic viability. As raw material cost constitute 35% to 80% of that of the finished article, the future of polymer blends lies in their attractive cost/performance ratio. An expensive polymer whose property spectrum is high, needed for a new application may be blended with an inexpensive polymer whose property spectrum is such that the resulting polymer blend has a cost to performance ratio that makes it very attractive for the given application. Thus, the standard of performance demanded by the new application is satisfied by a mixture of commercially available polymers without the need to develop a new polymer or to invest in a new plant.

The primary advantages in employing polymer blends or alloy are higher performance at a reasonable price, modification of performance as market develops, extending the performance of expensive resins, re-use of plastic scrap, generation of a unique material as far as its processability and/or performance are concerned. Now a days the release profile of a drug formulation are controlled through the use of biocompatible polymer blends [99, 100].

Generally, blending technology rests on the premise of property additivity [58], although the additivity principle is not strictly valid for most polymer blends. Wherever additivity properties are valid, one can prepare tailor-made materials by selecting the appropriate quantity of the components in the polymer blends. Multiphase polymer blends (immiscible polymer blends) have assumed greater commercial importance than miscible polymer blends [101]. Because of the success of these commercial polymer blends, attempts are being made to modify the mechanical response of normally immiscible polymer blends by adding the agents that could guarantee good stress transfer between the components of the multi component multiphase polymer blends.

X. WATER SOLUBLE POLYMERS

Importance of water soluble polymers

The work on water soluble polymers is the most fascinating and hence more advanced studies on their properties and biomedical applicability are in progress where the advantage of water as a solvent can be employed. Water soluble resins are used in almost every branch of industry [102]. However water soluble polymers are not the most glamorous of polymers. They are not in the public eye as are the more exotic polymeric products, such as nose cones for missiles, nylon for paint brushes, poly (vinyl chloride) for cosmetic jars and bottles, cables and pipes and polystyrene handles for toothbrush. Yet these water soluble polymers perform essential functions in biomedical/biological systems, latex paints, adhesives, cosmetics and foods. This lack of public awareness however does not change the fact that water soluble polymer business represents a sizeable and steadily growing segment of the industry. It has been found that the total world production of water soluble polymers is more than five million tons/year, of this, some 80 – 90% is carbohydrate based (including starch and natural gums) with an additional 3 lakhs tons/year of cellulose ethers, about 1 lakh tons/year of proteins, the remaining being synthetic

polymers, the most important of which are poly (vinyl alcohol) and polyacrylamides. Water soluble polymers are therefore of considerable economic importance, and the industries, in which they are used, including pharmaceutical, paper coating, textile sizing, detergent production, water treatment and oil-well drilling, have a significant effect on our daily life [102, 103].

Classification of water soluble polymers

The water soluble polymers are most important from both scientific and technological aspects. Water soluble polymers are classified according to their origin into three main types as follows [104]: (i) Natural products (biopolymers), (ii) Modified natural products (semi-synthetic water soluble polymers), and (iii) Synthetic water soluble polymers. Biopolymers are defined as polymers formed under natural conditions during the growth cycles of all organisms. Natural products or biopolymers are derived from animal and vegetable sources and have been marketed for many years. They are formed within cells by complex metabolic processes. They represent by far the largest volume of sales in the water soluble polymer area. For materials applications, cellulose and starch are most interesting. However, there is an increasing attention in more complex hydrocarbon polymers produced by bacteria and fungi, particularly in polysaccharides such as Xanthan gum, Guar gum, curdlan, Pullulan, etc. Modified natural products or semi-synthetic water soluble polymers are the compounds produced by altering the chemical structure of biopolymers. This class of polymers is represented by the alkyl and hydroxyalkyl ethers of cellulose and starch, ionic starches – starch sulphates, sulphonates and carboxylates – carboxymethylcellulose and the mixed ethers of starch and cellulose. Synthetic water soluble polymers are the latest members of the water soluble polymer family. Some of the examples are poly (vinyl alcohol), poly (vinyl pyrrolidone), and poly (vinyl methyl ethers), polyacrylic acids and its salts, polyacrylamides, ethylene oxide polymers and various copolymer systems.

Applications of water soluble polymers/blends

The semi-synthetic and synthetic water soluble polymer market is growing at a higher rate because they are not only displacing biopolymers in many applications, but are also creating entirely new end-use areas. Even though higher priced, they are replacing natural products because of greater efficiency (much lower dosages are needed to do a given job), increased versatility (they can be tailored to serve better in a given need) and lower biological oxygen demand (important where stream pollution is in a critical consideration) [102-106]. Water soluble polymers are used in three main areas: medical, agricultural and goods packaging. Intensive research in these fields has resulted in the development of commercial products. Because of their high specialization and greater unit values, medical applications have developed more rapidly than the others. These developed biodegradable synthetics serve as surgical implants in the blood vessels, in orthopedic surgery as implantable matrices for controlled long – term drug release in an organism, and as absorbable surgical sutures, as well as for eye treatment. Water soluble polymers can be derived from synthetic, semi-synthetic or natural sources. As with many macromolecules, the differing stereochemistry of these high molecular weight compounds results in multiple arrays of primary, secondary, and tertiary/quaternary composites within their structure. However, regardless of their inherent structural complexity, water soluble polymers are commonly biocompatible and, in



most cases, biodegradable. Their low environmental burden makes it suitable for wide range of applications within the textile, food, healthcare, paper, adhesive, waste treatment, oil recovery, thin film and wrap sizing industries.

Recently the term “biomaterial” has been defined as a non - living material used in medical device applications for interaction with a biological system. It is important that the term “biocompatibility” was also formulated; it determines how a tissue responds to foreign material. Biocompatibility is the ability of a material to coexist with some host’s reactions in a specific use. The important applications of some water soluble polymers in various fields [102-111] are given in Table 2 and some functions of water soluble polymers and their uses are given in Table 3

Table 2: Important applications of water soluble polymers

Important area of use	Some of the water soluble polymers used
Adhesives, bonding agents and glues	PVA, polyacrylic acid salts.
Agricultural and horticultural products	Polyacrylamide, PEO, PEG, gum arabic, Guar gum, alginates, agar-agar.
Asphalt emulsions and pitches	HPMC, guar-gum, alginates.
Beverages and foods	HPMC, MC, gum arabic, gum tragacanth, Guar gum, locust bean gum, starch, agar-agar, alginates, casein, gelatin.
Cements, concrete, plasters, ceramics and glazes	HEC, HPMC, MC, polyacrylamide, acrylamide copolymers, PVA, gum arabic, alginates.
Detergents, emulsifier formulations and laundry products	HEC, PEG, PEO, PVP, carboxyvinyl polymer.
Flocculation	Polyacrylamide, PEO, Guar gum, starch derivatives, alginates, gelatin.
Inks, paints and other surface coatings	HEC, PEG, PEO, PVA, PVP, gum arabic, cellulose ether, MC, polyacrylic acid salts, polyacrylamide.
Mining and mineral processing	HEC, Guar gum, agar agar.
Oil- well drilling and oil –recovery	HEC, HPMC, PEO, starch derivatives.
Paper, wall paper, wall board production	HEC, HPMC, MC, acrylamide copolymers, PVA, PVP, gum arabic, gelatin, starch, agar-agar, casein.
Pharmaceutical, dental & related products	HEC, MC, PEG, PEO, PVP, gum arabic, gum karaya, Guar gum, locust bean gum, starch derivatives.
Photographic films and related products	HEC, PEO, PVA, agar agar, alginates, gelatin.

Table 3: Some functions of water soluble polymers and their uses

Important function	Uses
Thickening and gelling	Bacteriological and microscopy media; cosmetics and toiletries;



	drilling muds for oil products, dye pastes (textile printing), foods, glazes, links, lattices, lubricants, paints, pharmaceuticals.
Stabilizing agents and suspensions	Cosmetics and toiletries, detergent formulations, drilling muds for oil production, emulsion polymerization, foods, glazes, ink, paints, pharmaceuticals.
Flocculating and clarifying suspensions	Beverages, mineral procession, water treatment.
Coatings, films and sheets	Laundry bags, mould release agents, oil-resistant films, packaging (single-dose products), photographic films, temporary protective coatings, textiles (warp-size agents).
Solid –solid bonding	Adhesives, agricultural and horticultural sprays, cements, ceramics, explosives, fertilizers, foundry cores and moulds, hair sprays, leather processing, paper production, pharmaceuticals.
Moisture retention (humectants)	Foods, lather processing, tobacco products.
Osmotic effects	Blood-plasma substitutes, cryoprotectants.
Complexing	Dye-leveling and dye-stripping (textiles), pharmaceuticals, tannin precipitation (beverages).
Crystal-growth modification	Cryoprotectants, electroplating and electro-refining, foods, pharmaceuticals.

XI. CONTROLLED DRUG RELEASE SYSTEMS

For many decades treatment of an acute disease or chronic illness has been mostly accomplished by delivery of drugs to patients using various pharmaceutical dosage forms, including tablets, capsules, pills, suppositories, creams, ointments, liquids, aerosols and injectables, as drug carriers. Even today these conventional drug delivery systems are the primary pharmaceutical products commonly seen in the prescriptions and in the market. This type of drug delivery system is known to provide a prompt release of drug. Therefore, to achieve as well as to maintain the drug concentration within the therapeutically effective range needed for treatment, it is often necessary to take this type of drug delivery system several times a day [112-114].

The restrictions of classic methods for drug administration (by injection or tablet) are widely known. As a dose is applied, the plasma levels will go up, but they will fall drastically when the drug has been metabolized and soon be below therapeutic level. The next dose will make the plasma level high again and a cyclical pattern may be established. The drug usually permeates throughout the body and is not targeted to the site where it is specifically required. Therefore, in classical drug administration, the drug concentration in plasma level swings above the maximum level or a lack of efficiency if the drug falls below the minimum level. One of the possible solutions to this problem is to use a system of controlled drug delivery in which the drug is released at a constant, preset rate, preferably near to the specific location. One of the most preferred approaches is when the drug is contained in a polymer membrane (or encapsulated in a polymer matrix), from which it

diffuses out into the tissue. Since the initiation of pharmacological therapy, maintaining steady therapeutic drug concentration level while minimizing side effects has been major challenge. The ideal drug delivery system should be inert, biocompatible, mechanically strong, capable of achieving high drug loading, safe from accidental release, simple to apply and remove, ease to fabricate and sterilize and comfortable for the patient [112-115].

XII. POLYMERS IN CONTROLLED DRUG RELEASE SYSTEMS

Controlled release drug delivery system should necessarily consist of a barrier, which is generally a polymer. Naturally occurring polymers that are used in controlled release formulation may be obtained from plant extrudates (gum acacia, gum tragacanth, gum karaya, gum ghatti), seed or root (tamarind root, locust bean gum, orka gum), sea weed extract (chitin/chitosan, algin, carrageenan) and miscellaneous like pectin, gelatin and starch. Natural polymers have some disadvantages such as inappropriate mechanical properties, low strength, inconsistent behaviour and poor cell adhesion. To overcome these disadvantages semi-synthetic or synthetic polymers are employed. Some of the semi-synthetic polymers are cellulose based (methylcellulose, carboxymethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, hydroxyethylcellulose), starch based (dextrin, carboxymethylstarch, starch amylopectin, hydroxyethylstarch, hydroxypropylstarch) and miscellaneous like poly (propylene glycol), pectin, carboxy locust bean gum, carboxymethyl guar hydrogel, etc. Synthetic polymers which are generally employed in controlled formulations are vinyl polymers (PVP, PVA, carboxyvinyl copolymers), acrylic polymers (polyacrylic acid, polyacrylamide) and ethylene oxide polymers (polyox, various polaxamer) [116-129].

The miscibility nature of some biocompatible/biodegradable polymer blend systems studied by various investigators are shown in Table 4.

Table 4: Miscibility nature of some biocompatible/biodegradable polymer blends

Polymer Blends	Miscibility	Reference
Chitosan/gelatin	Immiscible	Basavaraju et al. [130]
Chitosan/PEG	Semi-miscible	Jayaraju et al. [98]
PLA/PEG	Semi-miscible	Mihir Sheth et al. [82]
CAP/PVP	Immiscible	Vijayalakshmi Rao et al. [122]
PVC/Starch	Immiscible	Thakora et al. [131]
PEO/PMMA	Miscible	Elberaich et al. [132]
PVP/PVA	Miscible	Vijayalakshmi Rao et al. [133]
PC/PEO	Immiscible	Varadarajulu et al. [134]
PC/PVP	Immiscible	Varadarajulu et al. [134]
NaAlg/PVA	Semi-miscible	Raviprakash et al. [135]
PSS/PVP	Immiscible	Garcia et al. [136]
PLL/PVP	Immiscible	Garcia et al. [136]
cellulose/alginate	Immiscible	Zhang et al. [137]

PVC/PVP	Miscible	Zheng et al. [138]
HPMC/PVP	Miscible	Amarakala et al. [139]
Hexanoyl chitosan/polylactide	Immiscible	Manisara Peesan et al. [140]
XG/gelatin	Semi-miscible	Basavaraju et al. [141]
Chitosan/HPMC	Semi-miscible	Jayaraju et al. [142]
Chitosan/PVA	Semi-miscible	Jayaraju et al. [143]
Chitosan /PVP	Semi-miscible	Jayaraju et al. [144]
Dextran/PVP	Miscible	Al-Khatani et al. [145]
HPMC/PEG	Semi-miscible	Sudhir R. Illiger et al. [146]
PESu/PPSu	Semi-miscible	George Papageorgiou et al. [147]
PESu/PBSu	Semi-miscible	George Papageorgiou et al. [147]
Starch-Cl/PCL	Miscible	Dong-Keon Kweon et al. [148]
HPMC/Pullulan	Semi-miscible	Prasad P. et al. [149]
Guar Gum/Pullulan	Semi-miscible	Bhavya B. B. et al. [150]
Pullulan/Polyacrylamide	Semi-miscible	Vishwanath et al. [151, 152]
Sodium alginate/Pullulan	Miscible	Prasad P. et al. [153]
Methyl Cellulose/PVA	Semi-miscible	Guru G. S. et al. [154]
PVP/Pullulan	Semi-miscible	Guru G. S. et al. [155]
Xanthan Gum/PVP	Semi-miscible	Guru G. S. et al. [156]
Pullulan/CMC	Semi-miscible	Guru G. S. et al. [157]
Guar Gum/CMC	Semi-miscible	Bhavya M. S. et al. [158, 159]
Guar Gum/PVA	Semi-miscible	Bhavya M. S. et al. [160, 161]

XIII. CONCLUSION

Synthetic and natural polymers are used for numerous applications in the biomedical field. However the properties of pure synthetic polymers and those of pure biological polymers alone are often inadequate to produce materials with good combination of chemical, mechanical, thermal, and biological performance characteristics. Though natural polymers (biopolymers) generally offer excellent biocompatibility but their mechanical properties are often very poor. Synthetic polymers generally have good mechanical properties but their biocompatibility is not satisfactory. Now a days, especially in biomedical and biotechnological fields, materials are required with good mechanical properties and good biocompatibility. Hence a set of new polymeric materials with desired properties have been prepared by blending synthetic polymers and biological macromolecules. Water soluble polymers like hydroxypropylmethylcellulose, pullulan, sodium alginate, xanthan gum, guar gum, carboxymethylcellulose, and poly(vinyl alcohol) has been studied by several researchers due to their blood compatibility, non-toxic, non-immunogenic, non-mutagenic and non-carcinogenic nature.



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REFERENCES

- [1] Tubbs R. K., *J. Polym. Sci.*, 4, (1966), 623–629.
- [2] Weintraub R. S., *Science*, 130, (1959), 711–713.
- [3] Knop K., Hoogenboom R., Fischer D., Schubert U. S., *Chem. Int. Ed.*, 49, (2010), 6288–6308.
- [4] Veronese F. M., Pasut G. *Drug Discovery Today*, 10, (2005), 1451–1458.
- [5] Chowhan Z. T., Amaro A. A., Ong J. T. H., *J. Pharm. Sci.*, 81, (1992), 290–294.
- [6] Reneker D. H., Yarin A. L., Fong H., Koombhongse S., *J. Appl. Phys.*, 87, (2000), 4531–4547.
- [7] Chowhan Z. T., *J. Pharm. Sci.*, 69, (1980), 1–4.
- [8] Ayers D., Cuthbertson J. M., Schroyer K., Sullivan S. M., *J. Control. Release*, 38, (1996), 167–175.
- [9] Saunders G., MacCreath B., *Biodegradable Polymers Analysis of Biodegradable Polymers by GPC-SEC. Application Compendium*, Agilent Technologies Inc.: Santa Clara, CA, USA, 2010.
- [10] Seong J. Y., Jun Y. J., Kim B. M., Park Y. M., Sohn Y. S., *Int. J. Pharm.*, 314, (2006), 90–96.
- [11] Singh A., Krogman N. R., Sethuraman S., Nair L. S., Sturgeon J. L., Brown P. W., Laurencin C. T., Allcock H. R., *Biomacromolecules*, 7, (2006), 914–918.
- [12] Penczek S., Duda A., Kaluzynski K., Lapienis G., Nyk A., Szymanski R., *Makromol. Chem. Macromol. Symp.*, 73, (1993), 91–101.
- [13] Kopecek J., Bazilova H., *Eur. Polym. J.*, 9, (1973), 7–14.
- [14] Penczek S., Klosinski P., *Synthetic Polyphosphates Related to Nucleic and Teichoic Acids. In Models of Biopolymers by Ring-Opening Polymerization*; Penczek, S., Ed.; CRC Press: Boca Raton, FL, USA, 1990; pp. 291–378.
- [15] Persigehl P., Jordan R., Nuyken O., *Macromolecules*, 33, (2000), 6977–6981.
- [16] Adams N., Schubert U. S., *Adv. Drug Deliv. Rev.*, 59, (2007), 1504–1520.
- [17] Oda T., Akaike T., Hamamoto T., Suzuki F., Hirano T., Maeda H., *Science*, 244, (1989), 974–976.
- [18] Morahan P. S., Munson J. A., Baird L. G., Kaplan A. M., Regelson W., *Cancer Res*, 34, (1974), 506–511.
- [19] Macfarlane G. T., Hay S., Macfarlane S., Gibson G. R., *J. Appl. Bacteriol*, 68, (1990), 179–187.
- [20] Chourasia M. K., Jain S. K., *J. Drug Target*, 2, (2004), 1–8.
- [21] Tomolin J., Taylor J. S., Read N. W., *Nutr. Rep. Int.*, 39, (1989), 121–135.
- [22] Bayliss C. E., Houston A. P., *Appl. Environ. Microbiol*, 48, (1986), 626–632.
- [23] Katzbauer B., *Polym. Degrad. Stabil.*, 59, (1998), 81–84.
- [24] Sharma B. R., Naresh L., Dhuldhoya N. C., Merchant S. U., Merchant U. C., *Food Promot. Chron.*, 1, (2006), 27–30.



- [25] Paoletti S., Chemistry and Function of Pectins; Fishman M. L., Jen J. J., Eds.; American Chemical Society: Washington, DC, USA, 1986.
- [26] Mukhiddinov Z. K., *Talanta*, 53, (2000), 171–176.
- [27] Roper H., *Carbohydr. Eur.*, 15, (1996), 14–21.
- [28] Zhang J. F., Sun X. Z., *Biomacromolecules*, 5, 2004, 1446–1451.
- [29] Araujo M. A., Cunha A., Mota M., *Biomaterials*, 25, (2004), 2687–2693.
- [30] Nabais T., Brouillet F., Kyriacos S., Mroueh M., Amores da Silva P., Bataille B., Chebli C., Cartilier L., *Eur. J. Pharm, Biopharm*, 65, (2007), 371–378.
- [31] Mulhbacher J., Ispas-Szabo P., Lenaerts V., Mateescu M. A., *J. Control. Rel.*, 76, (2001), 51–58.
- [32] Milojevic S., Newton J. M., Cummings J. H., Gibson G. R., Botham R. L., Ring S. G., Stockham M., Allwood M. C, *J. Control. Release*, 38, (1996), 75–84.
- [33] Rokhade A. P., Agnihotri S. A., Patil S. A., Mallikarjuna N. N., Kulkarni P. V., Aminabhavi T. M., *Carbohydr. Polym.*, 65, (2006), 243–252.
- [34] Okamoto H., Nakamori T., Arakawa Y., Iida K., Danjo K., *J. Pharm. Sci.*, 91, (2002), 2424–2432.
- [35] Li H., Guo L., Li J. W., Liu N., Qi R., Liu J., *Int. J. Oncol.*, 17, (2000), 927–932.
- [36] Abetamann V., Kern H. F., Elsasser H. P., *Clin. Cancer Res.*, 2, (1996), 1607–1618.
- [37] Clasen C., Kulicke W. M., *Prog. Polym. Sci.*, 26, (2001), 1839–1919.
- [38] Senel S., Hincal A. A., *J. Control. Release*, 72, (2001), 133–144.
- [39] Katzhendler I., Mader K., Friedman M., *Int. J. Pharm.*, 200, (2000), 161–179.
- [40] de Abreu F. R., Campana-Filho S. P., *Polímeros*, 15, (2005), 79–83.
- [41] Ge H. C., Luo D. K., *Carbohydr. Res.*, 340, (2005), 1351–1356.
- [42] Paulino A. T., Minasse F. A., Guilherme M. R., Reis A. V., Muniz E. C., Nozaki J., *J. Colloid Interface Sci.*, 301, (2006), 479–487.
- [43] Chen X. -G., Park H. -J., *Carbohydr. Polym.*, 53, (2003), 355–359.
- [44] Shengling S., Aiqin W., *React. Funct. Polym.*, 66, (2006), 819–826.
- [45] Shengling S., Wang L., Wang A., *J. Hazard. Mater.*, 136, (2006), 930–937.
- [46] Franssen O., Vandervennet L., Roders P., Hennink W. E., *J. Control. Release*, 60, (1999), 211–221.
- [47] Stenekes R. J. H., Franssen O., van Bommel E. M. G., Crommelin D. J. A., Hennink W. E., *Pharm. Res.*, 15, (1998), 557–561.
- [48] van Dijk-Wolthuis W. N. E., Hoogeboom J. A. M., van Steenberg M. J., Tsang S. K. Y., Hennink W. E., *Macromolecules*, 30, (1997), 4639–4645.
- [49] Simoes S., Slepshkin V., Pires P., Gaspar R., de Lima P. M. C., Duzgunes N., *Biochim. Biophys. Acta*, 1463, (2004), 459–469.
- [50] Peters T., Serum Albumin, *Adv. Protein Chem.*, 37, (1985), 161–245.
- [51] Brzoska M., Langer K., Coester C., Loitsch S., Wagner T. O., Mallinckrodt C., *Biochem. Biophys. Res. Commun.*, 318, (2004), 562–570.
- [52] Lui Y., Schnaram R., Reily W., *Pharm. Res.*, 14, (1997), 41-46.
- [53] Lev R., Long R., Mallonga L., Schnaram R., Reily W., *Pharm. Res.*, 14, (1997), 46-49.



- [54] W. J. Work, K. Horie, M. Hess, R. F. T. Stepto, *Pure Appli. Chem.*, 76, (2004), 1985-2007.
- [55] Hans Adam Schneider, *Polymer*, 30, (1989), 771-779.
- [56] O. Olabisi, L. M. Robeson, M. T. Shaw, *Polymer-Polymer Miscibility* (Academic Press: New York, 1979).
- [57] L. A. Utracki, *Polymer Alloys and Blends* (Hanser Publications, New York, 3, 1989).
- [58] Cowie J. M. G., *Miscibility in Encyclopedia of Polymer Science and Engineering* (Ed. Kroschwitz. Wiley Interscience Publication: John Wiley & Sons, New York, 1989).
- [59] J. Paul Flory, *Journal of Chemical Physics*, 10, (1942), 51-58.
- [60] S. Krause In: D. R. Paul, N. Seymour. Editors, *Polymer-Polymer Compatibility in Polymeric Blends* (New York, Academic Press, 1978).
- [61] P. L. Huyskens, W. A. P. Luck, T. Zeegers-Huyskens, *Intermolecular Forces* (Springer-Verlag: New York, 1991).
- [62] Y. P. Singh, R. P. Singh, *Eur. Polym. J.*, 20, (1984), 201-205.
- [63] Sonja Krause, *Pure and Applied Chemistry*, 58, (1986), 1553-1560.
- [64] J. N. Israelachvili, *Intermolecular and Surface Forces* (Second Ed., Academic Press: New York, 1991).
- [65] A. Leszek Utracki, *The Canadian Journal of Chemical Engineering*, 80, (2002), 1008-1014.
- [66] D. R. Paul, J. W. Barlow, *Journal of Macromolecular Science, Part C: Polymer Reviews*, 18 (1), (1980), 109-168.
- [67] R. Garcia, O. Melad, C. M. Gomez, J. E. Figueruelo, A. Campos, *Eur. Polym. J.*, 35, (1999), 47-55.
- [68] C. Rakkappan, S. Anbalagan, *American-Eurasian Journal of Scientific Research*, 4, (2009), 281-284.
- [69] S. M. Gheno, F. R. Passador, L. A. Pessan, *J. Appli. Polym. Sci.*, 117, (2010), 3211-3219.
- [70] Carla da Silva Meireles, R. Guimes Filho, M. N. Rosana de Assuncao, Mara Zeni, Katia Mello, *J. Appli. Polym. Sci.*, 104, (2007), 909-914.
- [71] L. Daniliuc, C. De Kesel, C. David, *Eur. Polym. J.*, 28, (1992), 1365-1371.
- [72] Y. P. Singh, R. P. Singh, *Eur. Polym. J.*, 19, (1983), 529-535.
- [73] R. N. Gupta, I. D. Gaba, C. D. Pande, Y. P. Singh, R. P. Singh, *Plenum Press*, 1, (1997), 547-552.
- [74] A. K. Kulshreshtha, B. P. Singh, Y. N. Sharma, *Eur. Polym. J.*, 24, (1988), 29-31.
- [75] Hani Younes, Daniel Coln, *Eur. Polym. J.*, 24, (1988), 65-72.
- [76] Jean Francois Masson, R. St. John Manley, *Macromolecules*, 24, (1991), 6670-6679.
- [77] D. J. Hourston, F. U. Schafer, *Polymer*, 37, (1996), 3521-3528.
- [78] D. J. Hourston, M. Song, A. Hammiche, *Polymer*, 38, (1997), 1-7.
- [79] Chee K. K., *Eur. Polym. J.*, 26, (1990), 423-428.
- [80] Sun Z., Wang W., Feng Z., *Eur. Polym. J.*, 28, (1992), 1259-1265.
- [81] E. Corradini, A. F. Rubira, E. C. Muniz, *Eur. Polym. J.*, 33, (1997), 1651-1657.
- [82] Mihir Sheth, R. Ananda Kumar, Vipul Dave, A. Richard Gross, P. Stephan Mccarthy, *J. Appli. Polym. Sci.*, 66, (1997), 1495-1505.
- [83] Z. Pingping, *Eur. Polym. J.*, 33, (1997), 411-419.
- [84] I. Katime, E. Diaz, R. Valenciano, *Eur. Polym. J.*, 34, (1998), 255-261.



- [85] A. Varadarajulu, R. Lakshminarayana Reddy, R. N. V. Ranga Reddy, *Acta Acustica*, 84, (1998), 577-579.
- [86] A. Varadarajulu, R. Lakshminarayana Reddy, Siddaramaiah, *J. Appli. Polym. Sci.*, 70, (1998), 1823-1827.
- [87] C. K. Yeom, K. H. Lee, *J. Appli. Polym. Sci.*, 67, (1998), 949-959.
- [88] J. He, W. Bu, J. Zeng, *Polymer*, 38, (1997), 6347-6354.
- [89] X. Chen, H. Hu, J. Yin, C. Zheng, *J. Appl. Polym. Sci.*, 56, (1995), 247-253.
- [90] S. Chattopadhyay, A. N. Banerjee, *J. Polym. Mater.*, 8, (1991), 351-362.
- [91] N. A. Mohamed, M. W. Sabaa, *Eur. Polym. J.*, 35, (1999), 1731-1739.
- [92] A. Elberaich, A. Daro, C. David, *Eur. Polym. J.*, 35, (1999), 1217-1222.
- [93] Yang Haiyang, Zhu Pingping, Wang Shiqiang, Guo Qipeng, *Eur. Polym. J.*, 34, (1998), 1303-1308.
- [94] W. H. Jiang, S. J. Han, *Eur. Polym. J.*, 34, (1998), 1579-1584.
- [95] S. Bagchi, S. K., Nema, R. P. Singh, *Eur. Polym. J.*, 22, (1986), 851-857.
- [96] S. D. Raviprakash, S. K. Rai, *J. Polym. Mater*, 22, (2005), 189-196.
- [97] K. C. Basavaraju, T. Damappa, S. K. Rai, *Carbohydrate Polymers*, 66, (2006), 357-362.
- [98] J. Jayaraju, K. C. Basavaraju, J. Keshavayya, S. K. Rai, *J. Macromolecular Sci., Part: B Physics*, 45, (2006), 741-751.
- [99] A. Merkli, C. Tabatabay, R. Gurni, J. Heller, *Prog. Polym. Sci.*, 23, (1998), 563-580.
- [100] Toshio, *Prog. Polym. Sci.*, 19, (1994), 663-702.
- [101] D. R. Paul, L. H. Sperling, Editors, Multi-component Polymer Materials, *American Chemical Society*, 211, (1985), 3-19.
- [102] Davidson R. L., Marshall Sittig, *Water – Soluble Resins (II Ed., Van Nostrand Reinhold Company, New York, 1968).*
- [103] Whisler R. L., *Industrial Gums (McGraw-Hill Book Company: II Ed. 1973).*
- [104] Davison R. L. *Hand Book of Water Soluble Gums (Academic Press: New York, 1980).*
- [105] Ida Vaskova, Pavol Alexy, Peter Bugaj, Anna Nahalkova, Jozf Feranc, Tomas Mlynsky, *Acta Chimica Slovaca*, 1, (2008), 301-308.
- [106] D. R. Lu, C. M. Xiao, S. J. Xu, *Express Polymer Letters*, 3, (2009), 366-375.
- [107] R. Chandra, Renu Rustgi, *Prog. Polym. Sci.*, 23, (1998), 1273-1335.
- [108] Long Yu, Yixiang Wang, Lina Zhang. *Biodegradable Polymer Blends and Composites from Renewable Resources, Chapter 6, Blends and Composites Based on Cellulose and Natural Polymers (John Wiley & Sons, Inc. 2009).*
- [109] Vipul Dave, Monica Tamagno, Bonaventura Focher, Enrico Marsano, *Macromolecules*, 28, (1995), 3531-3539.
- [110] Leathers T. D.: *In Polysaccharides and Polyamides in the Food Industry. Properties, Production, and Patents, 1: Polysaccharides; Steinbuchel A., Rhee S. K. (Eds.; Wiley-VCH: Weinheim, Chapter 11, 2005).*
- [111] *SBP Handbook of Industrial Gums and Resins (SBP Board of Consultants and Engineers, Delhi, 1998).*



- [112] Y. W. Chein, *Noval Drug Delivery Systems, Fundamentals, Developmental Concepts and Biomedical Assessments* (Dekker, New York, 1982).
- [113] Li Yan Qiu and You Han Bae, *Pharmaceutical Research*, 23, (2006), 1- 22.
- [114] M. Amelia Avachat, R. Rakesh Dash, N. Shilpa Shrotriya, *Ind. J. Pharm. Edu. Res.*, 45, (2011), 86-99.
- [115] A. Dash, G. C. Cudworth, *J. Pharmacological and Toxicological Methods*, 40, (1998), 1-8.
- [116] A. Abdel-Azim, Wagdy Y. Boutros, M. El-Sayed Abdel-Bary, *Polymer*, 39, (1998), 2543-2549.
- [117] Jean Francois Masson, R. St. John Manley, *Macromolecules*, 24, (1991), 6670-6679.
- [118] Chaobo Xiao, Hongjuan Liu, Yongshang Lu, Lina Zhang, *J. Appli. Polym. Sci.*, 81, (2001), 1049-1055.
- [119] Jun Wuk Park, Seung Soon Im, *Polymer*, 44, (2003), 4341-4354.
- [120] R. Paladhi, R. P. Singh, *Eur. Polym. J.*, 30, (1994), 251-257.
- [121] A. C. Wali, B. Vijaya Kumar Naidu, N. N. Mallikarjuna, S. R. Saikar, S. B. Halligudi, T. M. Aminabhavi, *J. Appli. Polym. Sci.*, 96, (2005), 1996-1998.
- [122] V. Rao, P. V. Ashokan, M. H. Shridhar, *J. Appli. Polym. Sci.*, 76, (2000), 859-867.
- [123] Changhua Liu, Chaobo Xiao, Hui Liang, *J. Appli. Polym. Sci.*, 95, (2005), 1405-1411.
- [124] S. A. Jones, G. P. Martin, P. G. Royall, M. B. Brown, *J. Appli. Polym. Sci.*, 98, (2005), 2290-2299.
- [125] Wei-Chi Lai, Wen-Bin Liau, *J. Appli. Polym. Sci.*, 92, (2004), 1562-1568.
- [126] Yasuyuki Agari, Kiyofumi Sakai, Yosikazu Kano, Ryoki Nomura, *J. Polym. Sci., Part: B Polymer Physics*, 45, (2007), 2972-2981.
- [127] Jun-Feng Su, Zhen Huang, Kai Liu, Ling-Ling Fu and Hong-Ru Liu, *Polymer Bulletin*, 58, (2007), 913-921.
- [128] Tuncer Caykara, Serkan Demirci, S. Mehmet Eroglu, Olgun Guven, *Polymer*, 46, (2005), 10750-10757.
- [129] C. Tonin, A. Aluigi, C. Vineis, A. Montarsolo, F. Ferrero, *Journal of Thermal Analysis and Calorimetry*, 89, (2007), 601-608.
- [130] K. C. Basavaraju, T. Damappa, S. K. Rai, *Carbohydrate Polymers*, 66, (2006), 357-362.
- [131] I. M. Thakore, Sonal Desai, B. D. Sarwade, Surekha Devi, *J. Appli. Sci.*, 71, (1999), 1851-1861.
- [132] A. Elberaich, A. Daro, C. David, *Eur. Polym. J.*, 35, (1999), 1217-1222.
- [133] V. Rao, P. Latha, *Journal of Materials Science Letters*, 18, (1999), 457-463.
- [134] A. Varada Rajulu, R. L. Reddy, *Intern. J. Polym. Mater.* 47, (2000), 469-475.
- [135] S. D. Raviprakash, H. V. Ramakrishna, S. K. Rai, A. Varada Rajulu, *J. Appl. Polym. Sci.*, 90, (2003), 33-38.
- [136] R. Garcia, C. M. Gomez, I. Porcar, J. E. Figueruelo, A. Campos, *Eur. Polym. J.* 33, (1997), 1723-1729.
- [137] L. Zhang, D. Zhou, S. Cheng, *Eur. Polym. J.*, 34, (1998), 381-388.
- [138] S. Zheng, Q. Guo, Y. Mi, *J. Polym. Sci.: Part B: Polymer Physics*, 37, (1999), 2412-2419.
- [139] C. Amarakala, B. S. Hiremath, K. Sherigara, K. Prashanth, Sheshappa Rai, S. Prasanna Kumar, *Ind. J. Chem. Techn.*, 9, (2002), 312-319.
- [140] Manisara Peesan, Pitt Supaphol, Ratana Rujiravanit, *Carbohydrate Polymers*, 60, (2005), 343-349.
- [141] K. C. Basavaraju, J. Jayaraju, S. K. Rai, T. Demappa, *J. Appli. Polym. Sci.*, 109, 2008, 2491-2497.
- [142] J. Jayaraju, S. D. Raviprakash, J. Keshavayya, S. K. Rai, *J. Appli. Polym. Sci.*, 102, (2006), 2738-2744.



- [143] J. Jayaraju, J. Keshavayya, S. K. Rai, K. C. Basavaraju, *J. Macro. Mol. Sci. Part A: Pure and Applied Chemistry*, 45, (2008), 271-279.
- [144] J. Jayaraju, J. Keshavayya, S. K. Rai, Shetty Ravindra Rama, *J. Macro. Mol. Sci. Part B: Physics*, 47, (2008), 296-302.
- [145] Al-Khatani Ahmed, J. Jayaraju, B. S. Sherigara, H. S. Naik Bhoja, J. Keshavayya, *J. Macro. Mol. Sci. Part A: Pure and Applied Chemistry*, 45, (2008), 1055-1062.
- [146] Sudhir Ramaswamy Illiger, Chandralekha Fadnis, T. Demappa, J. Jayaraju, J. Keshavayya, *Carbohydrate Polymers*, 75, (2009), 484-490.
- [147] Z. George Papageorgio, N. Dimitrios Bikiaris, *J. Polym. Sci., Part: B Polymer Physics*, 44, (2006), 584-597.
- [148] Dong-Keon Kweon, Norioki Kawasaki, Atsuyoshi Nakayama, Seiichi Aiba, *J. Appl. Polym. Sci.*, 92, (2004), 1716-1722.
- [149] Prasad P., Guru G. S., Shivakumar H. R., Sheshappa Rai K., *Journal of applied polymer science*, 110 (1), (2008), 444-452.
- [150] Bhavya B. B., Shivakumar H. R., Vishwanath Bhat, Prasad P., Guru G. S., *Malaysian Polymer Journal*, 8 (1), (2013), 33-37.
- [151] Vishwanath Bhat, Shivakumar H. R., Sheshappa Rai K., Ganesh Sanjeev, Prasad P., Guru G. S., Bhavya B. B., *International Journal of Polymeric Materials* 61 (4), (2012), 300-307.
- [152] Vishwanath Bhat, Shivakumar H. R., Sheshappa Rai K., Ganesh Sanjeev, Prasad P., Guru G. S., Bhavya B. B., *Journal of Macromolecular Science, Part A* 48 (11), (2011), 920-926.
- [153] Prasad P., Guru G. S., Shivakumar H. R., Sheshappa Rai K., *Journal of Polymers and the Environment* 20 (3), (2012), 887-893.
- [154] Guru G. S., Prasad P., Shivakumar H. R., Sheshappa Rai K., *Int. J. Res. Pharm. Chem.*, 2 (4), (2012), 957-968.
- [155] Guru G. S., Prasad P., Shivakumar H. R., Sheshappa Rai K., *International Journal of Plastics Technology* 14 (2), (2010), 234-245.
- [156] Guru G. S., Prasad P., Shivakumar H. R., Sheshappa Rai K., *Journal of Polymers and the Environment* 18 (2), (2010), 135-140.
- [157] Guru G. S., Prasad P., Shivakumar H. R., Sheshappa Rai K., *Malaysian Polymer Journal* 3 (2), (2008), 13-23.
- [158] Bhavya M. S., Savitha M. B., Prasad P., *International Journal of Advance Research in Science and Engineering*, 6(1), (2017), 514-523.
- [159] Bhavya M. S., Abhijith P. P., Sreelakshmi S. K., Savitha M. B., Prasad P., *International Journal of Advance Research in Science and Engineering*, 6(6), (2017), 572-578.
- [160] Bhavya M. S., Abhijith P. P., Sreelakshmi S. K., Savitha M. B., Prasad P., *International Journal of Advance Research in Science and Engineering*, 6(9), (2017), 1-8.
- [161] Bhavya M. S., Nagesh Bhat, Momin Ashraf, Krishnaraja Acharya, Savitha M. B., Prasad P., *International Journal of Advance Research in Science and Engineering*, 7 (1), (2018), 1-7.