**Advance Material Copolymers and Their Surface Modification Techniques: A Review**

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 **ABSTRACT**

The advancement in the science and technology allowed man to develop new materials i.e. polymers. Now polymeric materials are used in nearly all areas of daily life and their production and fabrication is done in major worldwide industries. Polymers have some limitations for their applications in different sectors, since most of them possess properties like stiffness and low strength.Then synthesize a polymer taking two or more different monomer units that is called copolymer. Enhance applicability of copolymer are depend there surface therefore very necessary to surface modification. Many different techniques for surface modification they are Wet Chemical Oxidation, Graft Polymerization, Plasma Surface Modification, Corona Treatment and Surface Coatings. In above method surface coating are simple, less energetic and very efficient techniques. Surface modification of copolymers has done by surface coatings with used of chemical or other polymeric material. Surface coatings are additional ways to modify surfaces of copolymers in an effort to increase their practical applicability. Surface modified copolymers are very efficient material which is use all areas of daily life.

**Keywords:-** Polymer, Copolymer, Techniques, Surface Modified Copolymer, Efficient Material.

1. **INTRODUCTION**

The advancement in the science and technology allowed man to develop new materials having desirable chemical, mechanical and electrical properties at room temperature as well as at higher temperatures and long periods of time without significant loss in its properties. The impact of this underscoped truth has vividly directed the attention of investigators to new materials i.e. polymers. The word *polymer* is derived from the classical Greek words *poly* meaning “many” and *meros meaning* “parts”. Simply stated, a polymer is a long-chain molecule that is composed of a large number of *repeating units* of identical structure. In other words polymers are high molecular mass substances consisting of large number of repeating structural units derived from simple molecules. They contain macro size molecule and have high molecular mass called macromolecules. The simple molecules which combine to give polymers are called monomers which are bonded covalently [1].

The birth of polymer science may be traced back to the mid-nineteenth century. In the 1830s, Charles Goodyear developed the vulcanization process that transformed the sticky latex of natural rubber into a useful elastomer for its use in making tire. In 1847, Christian F. Schon be in reacted cellulose with nitric acid to produce cellulose nitrate. This was used in the 1860s as the first man-made thermoplastic/celluloid. In 1907, Leo Hendrik Baekeland produced Bakelite from condensation of two chemical phenol and formaldehyde which was synthetic polymer available commercially in 1925. In 1912, Glyptal (unsaturated-polyester resin) was developed as a protective coating resin [2].In 1920s Wallace Carothers also demonstrates that polymer could be synthesized rationally from their constituent monomer. He invited first synthetic rubber called neoprene. In 1920s, Hermann Staudinger was the first to propose that polymers consisted of long chains of atoms held together by covalent bonds. For this work he received Nobel Prize in chemistry in 1953.[4] In the 1930s, researchers in the United States had produced a variety of new polymers including synthetic rubber and more “exotic” materials such as nylon and Teflon. In the 1936, polyvinyl chloride was used as a polymeric material. In 1938, Dow had produced polystyrene in commercial scale for the first time in Germany and in 1939, polyethylene (low-density) was made by scientists at ICI in England.Efforts to develop new polymeric materials, particularly synthetic rubber, were intensified during world war II when many naturally occurring materials such as hevea rubber were in short supply. In the1943, Polyolefins, polymers derived from olefins, were started to develop around 1950. In the 1950s, Karl Ziegler and Giulio Natta independently developed a family of stereospecific transition-metal catalysts that made possible the commercialization of polypropylene as a major commodity plastic [3].The first linear thermoplastic polycarbonate was commercially produced in 1960. Polypropylene was manufactured in 1962. The development and production of a new polymer is an extremely costly process, so the research on investigation of new methods for reducing the costs is important. For these reasons a great interest was developed during the 1970s and 1980s in the blending of polymers of different types to give either cheaper products or products with properties which were the combination of two or more polymers. The development of new polymers has not come to an end but polymer chemists continued to develop both new polymers and new polymerization processes. This leads to the introduction of polymers for special uses. Totally novel types of polymers have also been synthesized with a view to investigate whether they might have useful properties[4,5].

Hundreds of polymers have been synthesized and many more are likely to be produced in future. Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless forms and numbers because of very large number and type of atoms present in their molecule. Polymers can have different chemical structure, physical properties, mechanical behavior, thermal characteristics, etc.; and on the basis of these properties polymer can be classified in different ways [6,7].

1. **Properties of polymers**

 Every polymer has very distinct characteristics but most polymers have the general properties. Polymer properties are broadly divided into several classes. The most basic property of a polymer is the identity of its constituent monomers. The other one is the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major role in determining bulk physical properties of the polymer, which describes how the polymer behaves as a continuous macroscopic material. Chemical properties, at the nanoscale, describe how the chains interact through various physical forces. Some basic properties of polymers are very light in weight with great degrees of strength. Polymers can be processed in various ways. Polymers have many inherent properties that can be further enhanced.

Polymers can be very resistant to chemicals and also to weather. They only react with particular solvent. Polymer can act as both thermal and electrical insulator. Polymers have excellent transport properties such as diffusivity. Mechanical properties of polymers have made polymer to great interesting materials. Polymers replace many materials with their good physical properties. [8,9]

1. **Copolymer and their surface modification**

 Polymers have some limitations for their applications in different sectors, since most of them possess properties like stiffness and low strength. We can synthesize a polymer taking two or more different monomer units that is called copolymer. The copolymer can be obtained by addition or condensation polymerization. Addition polymerization results in chain growth while condensation result in step growth type of polymerization reaction. Most of these are obtained from condensation polymerization [10].During synthesis of copolymers we can have excellent control over the properties of bulk region. Bulk properties are desired properties for the copolymers because applications of copolymers depend upon these properties. Copolymer surface region many times may not possess desired properties for particular application which lead to their failure.[11]Surface modification of copolymer may enhance its applications. Few advantages of surface modification are permanent staining of fabric, delamination of adhesive bond, wet ability, reducing friction, coating application, dye adsorption, biomedical application and many more[12].

The copolymers have generally solvent resistant properties and lack of reactivity therefore specialized method is required to achieve the surface modification of copolymers. Many different methods for surface modification have evolved over the past fifty years[13,14]. They can be divided into three categories that are physicochemical method, mechanical method and biological method. The physicochemical methods are further subdivided into gas phase method which includes application of gases containing active species such as free radicals, electrons, ions and excited molecules or electromagnetic radiations, such as visible light, U.V. and gamma rays. Liquid and bulk phase method involves physical desorption from bulk phase or chemical reactions at the surface. The third one is combination of these two methods [15,16]. Mechanical method includes roughening (micro roughing to develop porous surface and micromanipulation) [17]. Biological method includes physical adsorption, self cross linking and chemical conjugation of biomolecules to the surface group (cell seeding and growth to confluence [18,19].

1. **METHODS OF SURFACE MODIFICATION OF COPOLYMERS**
2. **Wet chemical oxidation**

Wet treatment is also one of surface modification technique used in order to improve the surface of copolymer, in which the surface modification is done for conversion of nonpolar hydrophobic surfaces to polar hydrophilic and water wettable ones applying both physical and chemical methods. Copolymers surface composition is uniform thought out the surface. The amorphous and crystalline domains are present on it. The reactant usually behaves differently towards crystalline and amorphous domains. Thus the effect of wet treatment is not homogeneous on the surface. Most common wet treatments are the surface oxidation, surface etching and surface hydrolysis. Examples are, surface oxidation by treatment of copolymers using chromic acid solution, surface etching of fluoropolymer using sodium and surface hydrolysis of polyesters [20].

1. **Graft polymerization.**

Graft polymerization may introduce some desirable properties onto the surface of copolymer without change in the architecture of the copolymer backbone which leads to surface modification. Surface modification by polymer grafting has attracted particular attention of researchers. The common feature of the method is that an active site is created in pre-existing copolymer. The active site may be a radical or a chemical group which is involved during polymerization process. The conventional methods of graft polymerization are radiation, solution reaction and melt-mixing methods. Amongst these the melt–mixing method is considered as the most simple, economical, efficient and appropriate for industrial purposes [21,23].

1. **Plasma surface modification.**

 The treatment of polymeric materials with plasma is a frequently used technique to accomplish surface modification. Plasma can be used in many different cases wherever you like to modify the surface. There are two different plasma effects available that are low pressure plasma and atmospheric plasma. Low pressure plasma offers many versatile possibilities for surface modification. For example i) Cleaning of surface due to presence of any residues, oil or any contamination, ii) activation of various materials before gluing/ painting, iii) etching and partial removal of surface and iv) coating of parts with several possible types of layers that is protective barrier/friction reducing layer. Plasma treatment includes plasma surface modification using non polymerizable gases such as Ar, N2, and O2 etc[24,25].

1. **Corona treatment.**

 Corona treatment is surface modification method using a low temperature corona discharge to increase energy of a material, often copolymers and natural fibers. Corona discharge is generated when high-frequency, high-voltage, electricity from corona generator is applied between the electrodes and treating roller of the treating station using the plasma created to functionalize the surface. This treatment generally improves wettability and sometimes significantly improves i) the printing properties ii) coating properties iii) lamination properties. Properties of corona treatment are being applied for other purposes including oil film removal from metallic foil, anti-fog treatment of plastic boards[26,27]

1. **Surface Coatings**

Surface modification of copolymers has done by surface coatings with used of chemical or other polymeric material. Surface coatings are additional ways to modify surfaces of copolymers in an effort to increase their practical applicability. These techniques often do not involve direct attachment of chemical groups of the surface of copolymers. Surface coating of copolymers has been widened by suitable chemical modifications [28]. The chemical modification requires addition of chemicals or polymeric materials to interact with copolymer. The chemical used for surface modification of copolymer are easy to operate, low maintenance costs, low energy requirements, generate no toxic slurries and has high removal efficiency for heavy metals and dyes [29]. The biomaterial like chitosan also have similar characteristics such as low mechanical resistance and high solubility in acid medium. The copolymers can be chemically and mechanically stabilized by doping chitosan for surface modification. The heavy metal and dyes adsorption by chitosan gets enhanced due to higher adsorption capacity. At optimum pH condition, in addition, the developed surface modified copolymers material exhibit good adsorption capacities than that without chitosan doping. Therefore, chitosan can be used as surface modification of new copolymers emploning physicochemical methods like molecular adsorption-deposition [30].

1. **CONCLUSIONSC**

Synthesis of copolymer could be successfully after increase their efficiency to surface modification can take place. Many different techniques for surface modification they are Wet Chemical Oxidation, Graft Polymerization, Plasma Surface Modification, Corona Treatment and Surface Coatings. In above method surface coating are simple, less energetic and very efficient techniques. Surface modification of copolymers has done by surface coatings with used of chemical or other polymeric material.Surface modified polymers is very efficient material for their applicability

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