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

**Dr. Sudhakar Shamrao Shende**

Department of Chemistry,

Late N.P. Whagaye Arts, Commerce and Science College, Lakhani, Dist- Bhandara-441804, India

***Author Email***: sudhakarshende31@gmail.com

**Dr. Sudhirkumar Maroti Maskey**

Department of Chemistry,

Yashwantrao Chawhan Arts, Commerce and Science College, Lakhandur, Dist- Bhandara-441803, India

***Author Email***: sudhirraj2011[*@gmail.com*](mailto:Sudhirraj2011@gmail.com)

**ABSTRACT**

The advancement in the science and technology allowed human to develop new materials i.e. polymers. Now polymeric materials are used in nearly all the sector of today’s 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 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**

Today for advancement in the science and technology allowed human to develop new materials having appropriate chemical, mechanical and electrical properties at room temperature as well as at higher temperatures. When change any physical or chemical properties 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 materials which are consists of large number of repeating monomer molecule or simple organic molecule called polymer. 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].

Polymeric materials are first synthesis in the mid of nineteen century. In the 1830s, Charles Goodyear prepared elastomers using natural rubber latex this elastomer for its use in making tire. In 1847, Christian F. takes natural monomers cellulose with nitric acid to produce cellulose nitrate which use in the 1860s as the first man-made celluloid. In 1907, Leo Baekeland synthesis Bakelite polymers from condensation of two monomers phenol and formaldehyde which was synthetic polymer available commercially in 1925. In 1912, Glyptal was making as a protective coating resin i.e. unsaturated-polyester resin [2].In 1920s Wallace Carothers first synthetic rubber called neoprene. In 1920s, Hermann Staudinger explains propose structure of polymer he received Nobel Prize in chemistry in 1953, according to then polymers was long chains of carbon atoms held together by covalent bonds.[4] In the 1930s, scientist in the USA has synthesis very applicative polymeric material nylon and Teflon[3]. Now a day hundreds of polymers have been synthesized by their novelty and different their application. Polymers can be synthesis by addition polymerization and condense polymerization.

1. **Properties and classification of polymers**

Every polymer has different physical properties, chemical properties, mechanical behavior and thermal characteristic. Polymer have many different from and verities therefore polymers are classified into different ways. Depending on their source or origin of polymers classified natural, synthetic and semi synthetic polymers [4]. On the basis of structure polymers are classified strait chain polymers, branch polymers and cross link polymers. In polymers, monomer molecule have different intermolecular forces they are classified elastomer, fibers, thermoplastic and thermosetting polymers [5]. Depending their biodegradable properties polymers are classified into biodegradable polymers and non biodegradable polymers. Same polymer have same type of monomer called homopolymers and different types of monomers are copolymers [6,7]

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 [7,8].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.[9]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[10].

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 [11,12]. 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 [13,14]. Mechanical method includes roughening (micro roughing to develop porous surface and micromanipulation) [15]. Biological method includes physical adsorption, self cross linking and chemical conjugation of biomolecules to the surface group (cell seeding and growth to confluence [16].

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 [17].

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 [18,19].

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 have different and veritable 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[20,21].

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[22,23]

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 [24]. 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 [25]. 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 [26].

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

**REFERANCES**

1. F.W. Billmeyer, *Text Book of Polymer Science*, 3rd Edn., Wiley Interscience,New York, 1994
2. C.E. Carraher,Mark, H. F., Polymer Chemistry: The Past 100 Years. Chemical Engineering News, p. 176. 1976
3. Morawetz, H., Polymers: The Origins and Growth of a Science. New York: John Wiley & Sons. 1985
4. Furukawa, F., Inventing Polymer Science: Staudinger, Carothers, and the Emergence of Macromolecular Chemistry. 1998
5. M.P. Stevens, *Polymer Chemistry*, 3rd Edn., Oxford University Press, New York 1999
6. D.W. Van Krevelen, *Properties of Polymers*, 3rd Edn., Elsevier, New York,2000
7. G. Odian, *Principles of Polymerization*, 4th Edn., Wiley Interscience, New York 2004.
8. Luzinov, I.,; Iyer, K. S., Zdyrko, B.; Klep, V. Invention Disclosure: “Surface Treatment of Polymeric and Inorganic Surfaces”, February 2003.
9. L. E. Rentz, "Proper Surface Preparation," Adhes. Age p. 10 , 1987.
10. H. A. Willis and V. J. 1. Zichy in D. T. Clark and W. J. Feast, eds., Polymer Surfaces, Wiley, New York, p. 287., 1978.
11. Danilish, M.J. , et al. , J. Biomtls.sci. , Polym. Ed. , 1994 , 52, 35-53
12. Uchida ,E. , Uyama y . and Ikada Y. , J. Appl. Polym. SCi. , 1988 , 47 , 417
13. Iyer, K. S.; Luzinov, I. Surface Morphology of Mechanically Heterogeneous Ultrathin

Polymer Films, *Langmuir*, 19, 118. ( 2003 )

Harris , J. M. , ‘PEO chemistry , Biotechnology and biomedical application’ *Pllemum Press*, NY, 1992

Nagaosa , S., Shalaby .S.W. Hoffman ; Ratner B.D. and Horbett ,T. A. eds . ‘’Polymer as biomaterials’’ *Plenum press* .NY 1985

R. M. Podhany, "Comparing Surface Treatments," Converting pp. 48-52 , Nov. 1990

Draper, J.; Luzinov, I.; Tokarev, I.; Minko, S.; Stamm, M., Morphology and Wettability of Hybrid Polymer Brushes, *Polymeric Materials Science and Engineering*, 87 187 , 2002

Klep, V.; Minko, S.; Luzinov, I., Mixed Polymer Layers by "Grafting to"/"Grafting from Combination”, *Polymeric Materials Science and Engineering*, 89, 248. ( 2003 )

Lyer, K. S.; Zdyrko, B.; Malz, H.; Pionteck, J.; Luzinov, I. Polystyrene Layers Grafted to Macromolecular Anchoring Layer, *Macromolecules*, 36, 6519. 2003

Seidel, C., Kopf, H., Gotsmann, B., Vieth, T., Fuchs H. and Reihs, K.," Ar plasma Treated and Al Metallised Polycarbonate: a XPS, Mass spectroscopy and SFM study", *Applied Surface Science*, 150, 19-33 , 1999.

Shenton,M.J. and Stevens,G.C., "Surface Modification of Polymer Surfaces: Atmospheric Plasma versus Vacuum Plasma Treatments", *J. Phys. D: Appl. Phys*. (2001)., 34, 2761-2768

Abdrashitov E. F. and Ponomarev, A. N. "Plasma Modification of Elastomers", *High Energy Chemistry,* 37, 279-285 2003.

Markgraf, David A. *Corona Treatment: An Overview* Enercon Industries Corporation 1994.

J. DiGiacomo, Flame Plasma Treatment-a Viable Alternative to Corona Treatment, Society of Plastic Engineers Regional Technical Conference on Decorating and Joining of Plastics, , pp. 37-61. Sept.1995

Harris , J. M. , ‘PEO chemistry , Biotechnology and biomedical application’ *Pllemum Press*, NY, 1992

Kittur, F. S.; Prashanth, K. V .H.; Sankar, K. U.; Tharanathan,R. N. - *Carbohyd. Polym.*, 49, p.185 2002.