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Advancement in Technology through Graft Copolymerization

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A major part of the land on earth provides us renewable biomass that mostly degrades with time. Graft copolymerization is a chemical technique that improves the properties of the biomass and modifies its properties while sustaining the inherent trait. With the advancement of science and research many efforts have been made to modify the techniques for better scientific and industrial achievements. The review explores a brief overview of this magnificent engineering, various techniques, characterization and changes that have helped to provide useful results and develop the technology.

Our earth is rich in biomass and cellulose is its major constituent. Its structure consists of monomeric units of β-D-glucopyranose, linked through 1,4-β-glucosidic bonds. It undergoes photo-degradation, acid hydrolysis, oxidation and biodegradation [1]. The oxidation reaction of cellulose [2] involves the primary and secondary hydroxyl groups of the pyranose ring leading to carbonyl and carboxyl groups. When the oxidation is prolonged, depolymerization of cellulose and a general worsening of physical and mechanical properties of the material take place. Amongst various treatments used to improve the properties of natural fibers, graft copolymerization of vinyl monomers onto natural backbones seems to be an interesting tool to reduce the ageing in textiles, enhancing the mechanical properties and modifying the texture [1]. Graft copolymerization of vinyl monomers onto cellulose has been widely studied with numerous monomers [3-7].

The most abundant macromolecule on the earth is cellulose. Cellulose is a semi-crystalline polymorphic solid. Its tertiary structure reflects the arrangement of the molecules relative to each other in a state of aggregation whether it is amorphous or crystalline allomorph [8]. Various studies have been reported to explore the changes in the crystallinity [9] and thermal behavior [10] in regenerated cellulose. X-ray method has been the most important approach in estimating the proportions of crystalline cellulose. Bera et al. [11] reported that most important chemical groups in jute polymer are hydroxyl (-OH) and methylol (-CH_2OH). The hydroxyl groups in the non-crystalline region are more accessible and reactive than those in crystalline region. Jute was found to have a more complex structure as compared to cotton because of the presence of many hydroxyl groups [12-13]. Fernandez et al. [14] reported that thermal stability of the cotton could be improved on grafting. Thermal stability of cotton grafted with methylacrylate was higher than that of cotton grafted with vinyl acetate. Flax, hemp, pine needles, gum are some of the backbones which have widely been studied but it is hard to generalize the basic factor effecting the graft yield. The graft yield depends upon a number of physico-chemico-thermal factors like resonance, steric hindrance, polarity, energy that determine the surface grafting. The type of fiber, swelling, number of active sites, the nature and amount of the solvent and temperature of polymerization strongly influence the reactivity ratios. In absence of monomer rich phase, the diluents will compete with the monomers for adsorption sites. The amount of adsorption will depend upon the total amount of surface area present and this in turn, is dependent upon the rate of stirring. Physical factors like mixing efficiency determines the melt temperature, the pressure, the rheological properties, solubility of the initiator and the monomer. Elevated temperature favors the degradation, reduces the initiator half life, modifies the rate or specificity of the reaction, and influences the solubility and rheological parameters. Pressure, side products, unchanged monomers, solubility, volatility of the monomer, reactivity towards initiator, substrate derived radicals, susceptibility of the monomer to homo-polymers, partition coefficient of the initiator in the monomer and backbone, reactivity, specificity, side reaction, toxicity of the initiator and antagonistic effects of the oxidizer are some of the influencing factors [3-5,12,13].

The reactivity of monomers plays an important role in graft copolymerization, so different workers have studied the grafting of binary vinyl monomeric mixtures on backbone polymer [15]. The graft copolymerization of monomeric mixture is a more complex phenomenon than the grafting of the individual monomers due to their antagonistic or synergistic interactions resulting from the difference in reactivity ratios. Nurkelva et al. [16] studied the grafting of vinyl ether of monoethanol-amine in the presence of more active monomer, vinyl ether of ethylene glycol. Chemical nature, amount and properties like solubility of initiator, monomer and backbone determines the yield in chemically induced grafting. Several workers had studied the graft copolymerization of binary vinyl monomer mixtures on to cellulose, graft copolymers based on cellulose extracted from pine needles were synthesized by grafting of poly glycidyl methacrylate along with co monomers like acrylic acid, acrylamide and acrylonitrile by benzoyl peroxide initiation. Structural aspects of graft copolymers have been characterized and evaluated by elemental analysis, infra red studies and solvent uptake behavior. Various other scientists are using the advanced techniques such as FTIR, XRD, SEM, TEM, AFM, DSC, TGA and DTA for polymer characterization [17-24].

Radiation-induced graft copolymerization by binary mixtures of styrene and acrylamide onto cellulose acetate was carried-out by Bhattacharyya and Maldas [25]. The number, average molecular weights of the grafted chains were calculated and these were found to be dependent on monomeric composition. Radiation induced graft copolymerization of the individual monomer and co monomer mixtures of vinyl monomers onto polyester and cotton/polyester fabrics by the mutual method have been investigated. The effects of solvent, co monomeric mixture and radiation were examined [26].

Behavior and the properties of graft copolymers are related to the nature of the vinyl monomers incorporated into backbone to a large

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extent. It has been found that swelling behavior of the graft copolymers varies as a function of percentage grafting. Graft copolymers show higher swelling in dipolar protic solvents [27]. Numerous studies were performed to explore the factors that govern the swelling behavior of the wood by focusing on the properties of the impregnating solvents. Factors like dielectric constant, dipole moment, surface tension [28], amount, molecular weight [29,30], density [31] and hydrogen bond formation capacity of the solvent were screened [29]. However, temperature [32], dimension of the test specimen [30], intensity of the hydrogen bonds between the wood constituents [33] and the removal of extractives from the wood substrate were found to influence the swelling behavior [34]. Moisture absorbance, chemical resistance, dye uptake behavior, thermal resistance and swelling behavior are some of the properties that drastically change as a result of grafting, depending upon the graft yield [35-38].

So we have seen that the waste biomass present in abundance in nature can serve as a backbone that can be graft copolymerized by chemical or radiation means using various monomers to incorporate the desired physico-chemico-thermal modifications in nature and behavior of the fiber for better utilization in numerous application like packaging, insulators, biomaterials, transportation, aerospace and fiber reinforced composites due to better mechanical strength and viability. Graft copolymerization is a wise, economic and judicious means to utilize the renewable waste biomass.

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