

Reprocessing the Natural Fibers to Procure Advanced Materials

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Abstract

Nature and natural resources has offered the mankind with precious gifts for survival and maintenance but with the ever increase in population, pollution and deforestation the sustenance of natural resources is in suspicion. A major part of the land on earth provides us with renewable biomass that mostly degrades with time. Graft copolymerization is a chemical technique to improve the properties of the waste biomass and modify its properties while sustaining the inherent trait. With the advancement of science and research many efforts have been made to modify and improve the synthesis, characterization and evaluation techniques for a better scientific and industrial achievements. The review explores a brief overview of this magnificent engineering, its types and factors that has helped to provides with outstanding results.

Introduction

The word 'polymer' was derived from the classical Greek word 'poly' meaning "many" and 'meres' meaning "parts". If simply stated, polymers are large molecules formed by the repetition of small and simple chemical units called monomers. Polymers may be natural, synthetic or semi-synthetic in origin. They are synthesized by the process called polymerization and if the combining monomers which may be two or more, are different then the resultant is called copolymer. Lord Todd, President of Royal Society of London, answered to the question, 'What do you think has been the chemistry's biggest contribution to science, to society?' "I am inclined to think that the development of polymerization is, perhaps, the biggest thing chemistry has done, where it has the biggest effect on everyday life. The world would be totally different place without artificial fibers, plastics and elastomers. Even in the field of electronics, what would you do without insulation? and there you get back to polymers again" [1].

Cellulose has been the most abundant form of terrestrial biomass. It finds applications in many spheres of modern industry. Cellulose, especially cotton linters, has immense use in the manufacture of nitro cellulose, used in smokeless gunpowder. Cellulose could be processed to make cellophane and rayon and other textile derivatives. It has also been used in the laboratory as a solid substrate for thin layer chromatography and a major constituent of paper. In the recent years, many attempts have been made to modify cellulose by graft copolymerization of vinyl monomers that help in the incorporation of desirable properties without drastically affecting its inherent traits. The formation of graft copolymers with long polymeric sequences of diverse chemical composition opens the ways to afford specialty polymeric materials [2,3].

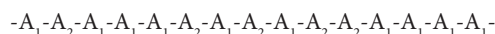
Concept of Copolymerization

A polymer may be known as homopolymer if it has similar monomeric units, whereas, if two different monomers are the repeat units, the resultant product is called copolymer and the reaction may be termed as copolymerization. Reactivity of a particular monomer decides the sequence in which the different monomers attach themselves onto the trunk polymer. Common methods to induce grafting are radiation source initiation, chemical initiation and physical or mechanical treatment (thawing or beating). Grafting may proceed either through ionic or free radical reaction mechanism.

Since the probability for the production of newer monomers at low cost remains bleak, so the modification of the synthetic and natural polymer through graft copolymerization, by incorporating specific properties through comonomers has gained much scientific attention. Improvement in dyeing, printing, chemical resistance, water repellency, fiber strength, abrasion resistance, crease resistance and impact strength of the thermoplastics and rubber are some of the advantages of the graft copolymerization. Sequencing copolymer exhibit many properties of each constituent homo-polymer. Copolymers with substantially large polymer sequences of diverse chemical compositions are designed in such a manner that the desirable properties are retained while eliminating the rest. Mechanical properties of polymers such as tensile strength, extensibility and impact-strength exhibit a correlation with the percent grafting (Pg). On grafting crystal lattice of the polymer gets disrupted but the strength of the added material helps to reinforce the structure. However, if crystallinity does not get distorted on grafting, then continuous increase in strength could be obtained with the increase in Pg [4,5]. Copolymers can be classified into different types:

Random copolymer

There lies no definite sequence of distribution of monomer units on the polymer back-bone. The monomer units are randomly placed along the polymeric chain and could be exemplified as:



Alternate copolymer

In these copolymers, monomers are placed orderly forming a polymeric chain and having a perfect alternate arrangement of monomer units, for example, poly (styrene-alt-maleic anhydride)

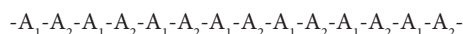
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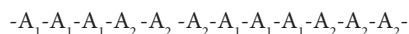
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where styrene (A_1) and maleic anhydride (A_2) are copolymerized in a regular fashion to give an alternate sequence as shown below:



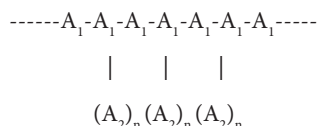
Block copolymers

They are composed of chemically dissimilar extended lengths or blocks or segments terminally connected to one another. They could be exemplified as:



Graft copolymers

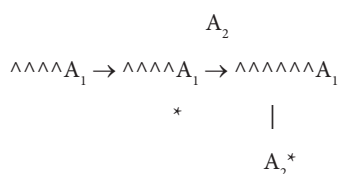
Graft copolymers involve a preformed polymeric back-bone to which other polymeric chains of different chemical nature get attached at several points. Stannett defined graft copolymers as: "Graft copolymers consist of a polymer back-bone with lateral covalently linked side chains." Both the back-bone and the side chain polymers could be homopolymers or copolymers. Graft copolymers are made of molecules with one or more block of species having different configurationally features connected to main chain as side chains [6]. Alfrey and Bandel [7] were the first to synthesize the graft copolymers in 1950. They polymerized vinyl acetate (VA) in presence of styrene (Sty) and vinylidene chloride (ViCl). The resulting graft copolymer assumed its shape depending upon the structural format of the back-bone polymer. The generalized view of graft copolymer has been shown below, where the monomer (A_2) has been incorporated onto the back-bone polymer, of building units (A_1).



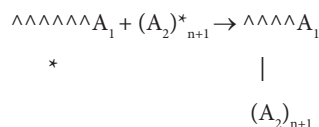
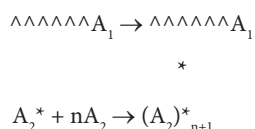
Monomer (A_2) could be grafted as a unitary system or as a binary mixture with other monomers. Although, random and alternate copolymers show better properties than the constituent homopolymers yet they are not found suitable for their applications as specialty polymers. On the other hand, both block and graft copolymers have been found to show many technologically advanced characteristics.

Grafting Methods

Induction of monomeric polymerization, if carried-out by an active site generated along a polymer back-bone, it is also called as 'grafting from' technique that finally ends in a graft copolymer:



Whereas, if there has been an attachment of the growing chain (A_2) onto polymer back bone (A_1), thereby, resulting in a graft copolymer, it may be named as 'grafting onto' technique:



Grafting could be achieved through free radical, anionic or cationic mechanism [1].

Synthesis of Graft Copolymers

Since last decades, numerous methods have been explored for the preparation of graft copolymers by conventional chemical techniques. The active sites are created on the polymeric back-bone for the synthesis of graft copolymers, either a free-radical or a chemical group that may get involved in an ionic polymerization or in a condensation process. Ionic polymerization has to be carried-out in presence of anhydrous medium or in presence of considerable quantity of alkali metal hydroxide. Usually, low molecular weight graft copolymers are obtained in ionic grafting, while in case of free radical grafting high molecular weight copolymers could be prepared [8-11]. A number of methods are used for the generation of active sites on the polymeric back-bone and are broadly classified as:

Physical methods

Active sites could be generated on the parent polymer by swelling it with suitable solvent that ruptures the bond leading to the formation of free radicals. Williams and Stannett [12] utilized freezing and thawing of polymer-monomer mixture to effect the grafting of vinyl monomers onto wool. Preparations of polymers with basic pendent moieties were carried-out by grafting dimethyl amino-ethylmethacrylate onto linear low density polyethylene (LDPE).

Chemical methods

Conventional radical initiators [13], benzoic peroxide (BPO), ceric ammonium nitrate (CAN) [14,15], potassium persulphate (KPS), Fenton's reagent (FAS- H_2O_2), potassium permanganate ($KMnO_4$), β -di ketones of transition metal alone and in conjugation with additives, Lewis acids, strong bases and metal carbonyl, have been successfully used for the chemical grafting similarly, Misra et al. [15-22] have successfully grafted a wide variety of monomers onto wool, cellulose, starch and gelatin by use of the radical initiators.

Physico-mechanical methods

In this method, the application of stress on parent back-bone caused segmental motions and molecular flow that leads to bond-scission and consequent formation of active sites on the back-bone. Free-radicals may also be generated by mastication and milling of back-bone polymers.

Radiation methods

The arena of graft copolymerization has been completely revolutionized by the radiation grafting of vinyl monomers onto the polymeric back-bone. When the electromagnetic radiations were passed through the reactants, there was a decrease in the intensity of the incident ray while the absorbed radiations created active sites on the polymer back-bone. Generally, UV and high-energy γ -radiations have been employed for generating the active sites where grafting of appropriate monomer takes place. In addition, low cost regulation over structural factors, such as the number and length of the grafted chain, has been done by careful selection of dose and dose rate [1].

Plasma radiation induced grafting

Plasma radiation induced grafting has gained much scientific attentions in the recent years. Plasma conditions attained through slow discharge offered the same possibilities as with ionizing radiation. Electron induced excitation, ionization and dissociation are some of the main processes. High energy accelerated electrons are the motivating agents that induce cleavage of chemical bonds in polymeric structure to form active sites.

Enzymatic grafting

In this method, an enzyme initiates the chemical or electro chemical grafting reaction [23], for example, phenol was converted to o-quinone by tyrosinase that underwent subsequent non-enzymatic reaction with chitosan. The enzymatic grafting on poly(dicarbazole-N-hydroxy-succinimide) film, thionine and toluidine blue have been inversely bound to the poly(dicarbazole) back-bone and grafting of polyphenol oxidase (PPO) on poly(dicarbazole) are some of the examples [1].

Factors affecting Graft Copolymerization

The percentage of grafting and grafting efficiency are usually affected by the nature of the monomer, concentration, reaction time, reaction temperature, reaction medium, additives and structure of the back-bone. Some of these factors affecting the graft yield have been discussed underneath [1,24]:

Role of inorganic ions on grafting

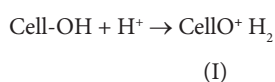
The free radical formation gets induced by the addition of some additives that increase the graft yield. In case of cellulose, Cu^{2+} ions help in complex formation. Only a small concentration of inorganic ions is needed to enhance the graft yield, whereas the higher concentration may adversely affect it. The effect of Cu^{2+} , Fe^{2+} , Fe^{3+} ions on radiation induced grafting in case of nylon was studied. The reactivity order observed was $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Fe}^{3+}$. Grafting efficiency of polar monomers was increased by facilitating monomer access on reaction site, by decreasing the crystallinity of cellulose and by the activation of the monomer through donor or acceptor complex formation with monomers after the addition of ZnCl_2 salt.

Different transition metals such as Zn, Fe, V, Co, Cr and Al have been used in the preparation of metal acetyl acetonates and other diketones. Metal acetyl acetonate could be used as an initiator for the vinyl polymerization. Metal chelates generally decompose on heating with the generation of free radicals that abstract hydrogen atoms from the polymeric back bone producing active sites.

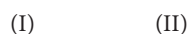
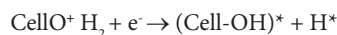
Metal chelates are better initiators as compared to other redox systems. Since the reaction could be carried-out even at low temperatures, so the undesired reactions due to chain transfer, homo-polymerization could be avoided [1].

Effect of acid in graft copolymerization

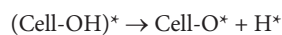
The strength of the acid used in the process has a great impact on the magnitude of graft yield. In radiation induced grafting of cellulose, following changes are supposed to occur [1,25]:



where, (I) could capture an electron to give (II).



Structure (II) decomposes into different radical species that offer sites for the attachment of graft chains.



Moreover, Cell and OH^* may also be formed depending on the dissociation point (II). H_2SO_4 has been reported to be the best acid amongst the series of acids to enhance the graft yield.

When Ceric Ammonium Nitrate (CAN) was used as a source of ceric ions, the presence of nitric acid has been found to play a significant role. In the absence of nitric acid no grafting was observed because of the large size ceric ions which were unable to form complex with the polymer back-bone. However, an increase in concentration of nitric acid resulted in the formation of complexes with functional groups on the polymer back-bone. The complex later decomposes to give free radicals on the back-bone where the grafting occurs [25].

Nature of the substrate

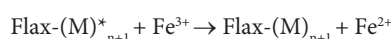
The rate of grafting has been found to increase with the increase in the surface area of the backbone. Therefore, the nature of the substrate as fiber, film or powder form plays an important role. It was reported that grafting of styrene onto cellulose acetate film decreased with increase in thickness of the film. Moreover, in case of cellulose, lignins adversely affect graft yield. Polymer analogous reactions of cellulose also affect grafting efficiency and affect the properties like swelling behavior, redox nature or the complex forming ability. Sometimes the groups introduced on the polymer back-bone decrease the graft yield due to increase in hydrophobicity, that blocks the diffusion of monomer and the initiator to the active sites.

Type of monomer and its concentration

Presence of aromatic rings, monomer polarity and the length of alkyl chain are among the structural factors that affect the graft yield and graft efficiency. Decrease in grafting efficiency has been reported as a function of steric and polar group. They had reported the decreasing reactivity order of various acrylates as methylacrylate (MA) > ethylacrylate (EA) > butylacrylates (BuA) > methylmethacrylate (MMA). Moreover, in case of simultaneous irradiation method, if monomer has high sensitivity to radiation than back-bone polymer, homo-polymerization is favored instead of graft copolymerization. A higher concentration of monomer may result in increased polymerization but at the same time graft copolymerization may not be the preferred process. In case of a redox reaction, graft copolymerization always starts from complex formation between monomer and the substrate that depends upon the concentration of monomer [1,24].

Effect of initiator concentration

Initiator concentration plays an important role to determine the graft yield. Generally at a molar ratio of 1:6 of FAS: H_2O_2 maximum grafting was observed. However, further increase in the molar ratio deteriorated the graft yield. This could be due to the fact that at higher concentration more Fe^{3+} ions are produced that served as chain terminator [26].



The amount of initiator, monomer and the back bone polymer are the major factors responsible to determine the rate of grafting. There are

various empirical relationships governing the dependence of grafting efficiency on the initiator concentration. It has been observed that once a certain initiator concentration is achieved, higher concentration of initiator do not further effects the graft yield [27].

Solubility of the initiator in the grafting medium shows a profound impact on the yield. Ideally, the initiator should be highly soluble in grafting medium in order to initiate the grafting through monomers [28,29].

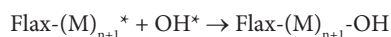
Effect of reaction temperature and reaction time

The graft yield gets enhanced with the increase in reaction time and temperature. After reaching the optimum value, further increase in either, results in the decline of percentage grafting. It occurs due to the increase in various hydrogen-abstraction reactions and high viscosity of the reaction medium, due to homopolymerization. High viscosity of the medium creates hindrance in the path of free radicals to reach the active sites on the polymer back-bone. Moreover, a further increase in temperature, results in the dissolution of water soluble components of the fiber thereby, affecting the overall graft yield [30-32].

Effect of the pH

The pH of the reaction medium plays a key role during the grafting process.

Kaith et al. [27] observed maximum graft yield at pH 7.0 and further increase in pH resulted in decreased graft yield. It could be due to decrease in the concentration of the free radicals on back-bone polymers as *OH ions served as the chain terminator [27]:



Effect of Grafting on the Properties of the Back-bone

The properties of the back-bone appreciably changes on grafting with vinyl monomers. As grafting involves covalent attachment of a monomer to a pre-formed polymeric back-bone, the physical nature and the chemical compositions play an important role in the process.

Grafting modifies the back-bone and makes it amorphous by the incorporation of monomer units. Grafting of hydrophilic monomers lead to increase in wettability, adhesion, dying and rate of release of oil stains. On the other hand, hydrophobic monomers affect the properties adversely. Grafting of acrylic acid (AA), methacrylic acid (MAA) and vinyl acetate (VA) onto the polymer back-bone increased water absorbance. Cellulose graft copolymers of styrene, acrylates and methyl methacrylate have been reported to be resistant to acids and imparted flame resistance to cellulose [33-36].

Graft Copolymerization onto Lingo-Cellulosics

Since the chapter deals with the grafting of vinyl monomers onto cellulosic fibers, so it was pertinent to discuss in brief the chemistry of cellulose and review of literature related to the modification of cellulose through graft copolymerization.

Cellulose has been the most abundant form of terrestrial biomass. It finds applications in many spheres of modern industry. Cellulose, especially cotton linters, has immense use in the manufacture of nitro cellulose, used in smokeless gunpowder. Cellulose could be processed to make cellophane and rayon and other textile derivatives. It has also been used in the laboratory as a solid substrate for thin layer chromatography and a major constituent of paper. In the recent

years, many attempts have been made to modify cellulose by graft copolymerization of vinyl monomers that help in the incorporation of desirable properties without drastically affecting its inherent traits. The formation of graft copolymers with long polymeric sequences of diverse chemical composition opens the ways to afford specialty polymeric materials [27,37,38].

So, we have seen above how the various researchers have utilized the low weight and high strength of natural fibers and polymers as backbone and graft copolymerized by various physico-chemical and radiation techniques using numerous monomers and characterization techniques to procure a number of modified graft copolymers. These graft copolymers are modified materials that can have desired physico-chemico-thermo-mechanical properties, depending upon the monomers and technique used. But, still a lot remains unexplored. Natural resources are the gift of the God to the mankind. But, with time these renewable resources and natural fiber will soon deplete. So, there is a great need to sustain and procure them for the future. They should be used economically and wisely. We should seek more fruitful means to explore the maximum potential and utilize the natural fiber for the development of science and technology [39-44].

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