CHAPTER - 1

INTRODUCTION TO GRAFT COPOLYMERS .

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In modern times polymers have made great impact on human life because of its use in every sphere of life. Polymers are not only used as commodity plastics, but are finding increasing usefulness in engineering applications due to factors such as lightness, low cost and ease of fabrication.

In 1909, the first ever commercial polymer 'Bakelite' that could be moulded in to hard infusible articles was prepared. In 1912, Jacques Brandenbarger introduced a famous transperent material 'Cellophene'. Within a decade several polymers started appearing and since then the scientific study and research in polymers have been ever growing areas.

1.1 WHAT ARE THESE POLYMERS ?

According to IUPAC definition "a polymer is a substance composed of molecules characterised by multiple repeatation of one or more species of atoms or groups of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with addition or removal of one or few of the constitutional units".

More simply a polymer is a long molecule built up by the repeatation of small simple chemical units held together by primary covalent bonds along the molecule.

1.1.1 Classification of polymers

Polymers can have different chemical structures; physical, mechanical behaviour; thermal characteristics etc. and can be classified in different ways, as discussed here.

1.1.1.a Accroding to 'origin' polymers are classified as

(i) Natural polymers and
(ii) Synthetic polymers

(i) Those isolated from natural materials are called as natural polymers, e.g., cotton, wool, silk and rubber.

(ii) Polymers synthesised from low molecular weight compounds are called synthetic polymers, e.g., polyethylene, polypropylene, nylon, poly (vinyl chloride).

1.1.1.b Considering the nature of the polymer backbone polymers are divided into

(i) Organic polymers and
(ii) Inorganic polymers

(i) A polymer whose backbone chain is essentially made of carbon atoms is termed as organic polymer. The majority of synthetic polymers are organic in nature and have been extensively studied.

(ii) The molecules of inorganic polymers generally contain no carbon atom in their backbone, e.g., glass and silicon rubbers.

1.1.1.c Polymeric materials are also classified into two groups according to their thermal responses

(i) Thermoplastics and

(ii) Thermosets

(i) Thermoplastic (also referred as thermosoftening) polymers soften on heating and stiffen on cooling. The process of heating and reshaping and retaining the same on cooling can be repeated several times. e.g., polyethylene, polypropylene.

(ii) Thermosetting (also referred as thermohardening) polymers undergo some chemical changes on heating and convert themselves into infusible mass which cannot be reshaped. e.g., Phenol-formaldehyde resins, vulcanized rubber, Silicon elastomers.

There are many advantages of synthetic polymers over natural polymers and hence further discussion is restricted only to synthetic organic polymers.

1.1.2 Why modify polymers ?

Polymers have their own characteristic properties and disadvantages e.g., polypropylene is hydrophobic, difficult to dye; nylons are very sensitive to moisture; rubbers are highly elastic; some polymers are brittle; some are rigid, whereas some have very poor mechanical and thermal properties. For specific applications, combination of various properties to different extent is required. Hence, ever increasing demand for newer products and appliances has kept process of modification of existing polymers and development of newer materials as an active research area. A great amount of research has been published in this area [1,2].

1.2 WHY MODIFY POLYPROPYLENE (PP) ?

Polypropylene is classified as a synthetic organic thermoplastic material and has occupied a prominent position because of its growing commercial applications. Over the recent years, a large number of novel materials based upon polypropylene blends have been introduced commercially to expand the property range of conventional PP [3-5]. However, this polymer has some drawbacks:

- it does not contain any reactive groups or sites;
- it has extremely poor hygroscopicity;
- it is difficult to dye;
- it has low melting and sticking temperatures and
- it is sensitive to photooxidation.

This restricts its use in several technologically important fields. Various attempts have been made to overcome these drawbacks. One of these is preparation of blends or alloys. But polypropylene due to its high molecular weight, crystallinity and hydrocarbon nature is incompatible with most of other polymers. Hence, it needs modification of its original properties before it can be used for blend/alloy preparation. Several methods are available for modifying polypropylene of which copolymerisation has proved an attractive means because the polymer not only retains most of its original properties but also precisely acquires some additional properties needed for a particular application.

Polypropylene can be degraded thermally as well as photochemically. The backbone of polypropylene possesses a hydrogen atom on a tertiary carbon atom and it has been observed that this tertiary hydrogen atom is involved in the degradation of a macromolecular chain. Hence, removal of this hydrogen atom during graft copolymerisation with a wide variety of monomers provides a powerful method for partial modification of polypropylene and improves its thermal and photochemical stability, dyeability and mechanical properties.

Here we have discussed different types of copolymers and copolymerisation processes, but our main emphasis is on graft copolymers.

1.3 COPOLYMERISATION

Polymeric substances containing two or more chemically different repeating units are termed as copolymers.

Simultaneous polymerisation of two or more monomers or one polymer and one monomer or two polymers in the given reaction mixture, to produce copolymers is termed as copolymerisation. Copolymerisation is the most general and powerful method of achieving desirable changes in polymer properties and is widely used in the production of various commercial polymeric materials. Copolymerisation influences the symmetry of the polymer chain and modulates both intermolecular and intramolecular forces and hence alters the properties such as melting point, glass transition temperature, crystallinity, stability, elasticity, permeability and chemical reactivity. There is practically unlimited scope for variation in polymer structure and polymer properties through copolymerisation.

1.3.1 Classification of copolymers

Classification of copolymers based on the morphology and arrangement of the monomeric units in the copolymer is as follows,

(i) Random copolymers: in which the distribution of two repeating units in the polymer is in a statistically random fashion along a linear chain.

-A-B-B-A-A-A-A-B-B-B-A-B-B-B-

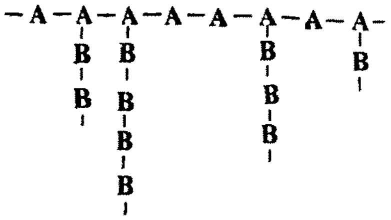
(ii) Alternating copolymers: in which the two repeating units are distributed alternately throughout the polymer chain.

-A-B-A-B-A-B-

(iii) Block copolymers: in which a sequence or block of one unit is followed by a block of other repeating unit and so on.

-A-A-A-B-B-B-A-A-A-

(iv) Graft copolymers : in which long or short chains of one type of monomer units are attached to a polymer backbone consisting of another repeat unit. This copolymer has different configurational features from other copolymers. The backbone and side chains may be homopolymeric or copolymeric units.



1.3.2 Graft copolymers

Graft copolymerisation is a well known method for modification of chemical and physical properties of polymeric materials [6,7] and is of a particular interest for achieving desired properties without altering the core structure of substrate. Usually main chain and branch chains are thermodynamically incompatible. Most of the graft copolymers can be classified as multiphase polymers in solid state, analogous to polymer blends, blocks and interpenetrating polymer network [8]. Macrophase separated graft copolymers can exhibit many of the unique thermal and mechanical properties observed in block copolymers, including thermoplastic elasticity. There is similarity in processing and fabrication of graft copolymers and many other polymeric materials. The graft copolymers have a greater sensitivity towards processing and fabrication due to their multicomponent nature. Grafting improves adhesion, tensile strength, abrasion resistance and dyeing and dye retention capacity of the copolymer. Grafting also improves compatibility and thermal as well as photochemical stability.

1.3.3 History of graft copolymers

Graft copolymers were unknowingly prepared by the chain-transfer mechanism in the early 1930's during investigations on the polymerisation of liquid vinyl monomers containing dissolved rubber [9,10]. The ability of a growing polymer chain to attach to a preformed chain of the similar type was recognised as early as 1933 [11] and this type of graft polymer reaction was clearly defined by Flory in 1937 [12] in treatment of kinetics of free radical polymerisation reactions [13]. The first all-synthetic graft copolymer prepared by transfer mechanism and characterised was poly (methyl methacrylate-g-p-chlorostyrene), reported in 1946 [14,15].

1.3.4 Methods of graft copolymerisation

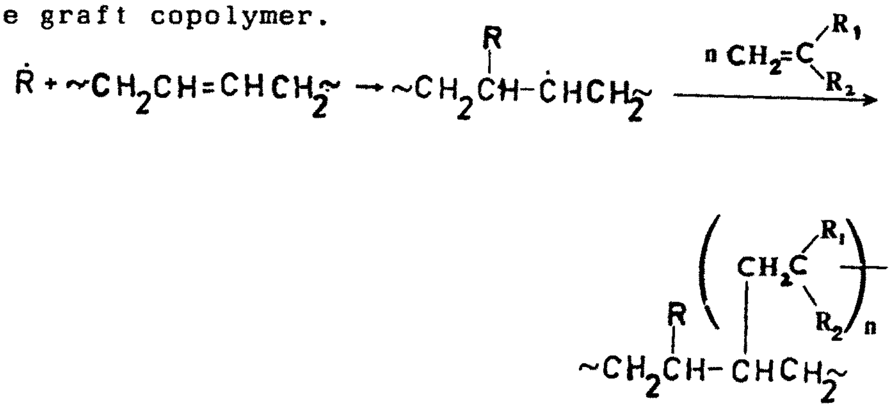
Formation of graft copolymers usually involves diffusion of monomer across the polymer backbone. The following methods can be used for synthesis of graft copolymers.

1.3.4.a Free radical mechanism

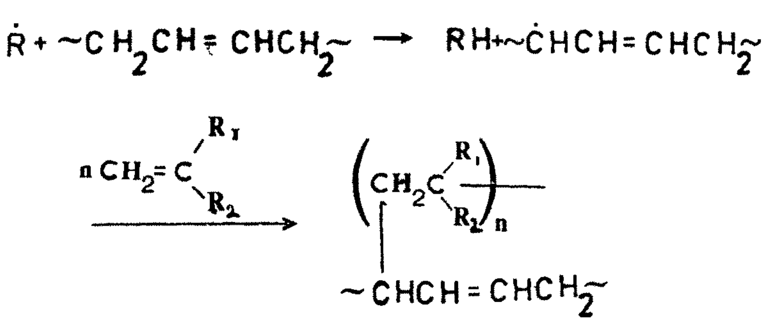
The free radical polymerisation is the oldest and most widely used procedure for the synthesis of graft copolymers.

There are five methods of grafting a polymer by free radical polymerisation technique.

(i) Chemical method : Graft copolymerisation through chemical initiation takes place by decomposition of the added initiator such as benzoyl peroxide, lauroyl peroxide, dicumyl peroxide etc., [16] which abstract hydrogen atom from the polymer chain to yield a free radical site for the graft copolymerisation of monomer unit. This is also called as chain transfer reaction. The radical, generated from decomposition of initiator, may attach to an in-chain double bond to add monomer to form the graft copolymer.



Or it may abstract an allylic hydrogen forming an allylic radical which subsequently adds monomer.



The efficiency of an initiator is an important factor in graft copolymerisation. The nature of monomer also plays an important role and success of chain transfer method to produce graft copolymers depends upon the relative reactivity ratios of monomers in the copolymerisation system.

(ii) Photochemical method : The chromophoric groups in the polymer absorb electromagnetic radiation in the visible and U.V. region. This results in bond breaking and subsequently in free radical generation which in turn may lead to initiate the grafting [17]. If the polymer is non-absorbing, indirect photolysis is initiated by using photosensitizer which absorbs the light and transfers this light energy to the polymer molecule present in the system, thus activating the molecule to give rise to free radical sites for the reaction.

(iii) Radiation induced grafting : In this method graft copolymerisation starts at radical sites generated along the polymer back bone due to high energy radiation e.g., gamma rays. The main disadvantages of this technique are crosslinking, homopolymerisation and degradation of the polymer backbone during grafting. In pre-irradiation technique, free radicals are trapped when the polymer is irradiated in the absence of air and afterwards monomer is introduced into the system to graft onto polymer backbone. Sakurada et al. [18], have grafted polystyrene onto cellulose fiber by this technique in dry air and confirmed that grafting occured by trapped radicals and not by peroxide group.

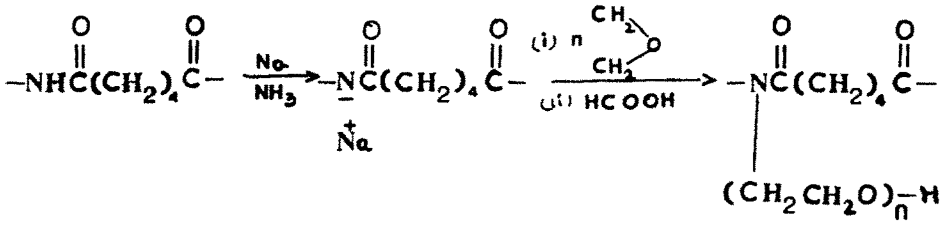
(iv) Plasma grafting : The grafting of plastics as well as naturally occuring fibers by glow discharge is known as plasma grafting. The exposure of polymers to glow discharge produces free radicals on the polymer backbone, which subsequently adds monomer as graft chain. A low temperature discharge is a complex system consisting of electrons, atoms, ionised species and excited atoms and molecules. These particles cause radiation effects on the surface of the material as well as in the interior of the substance. Millard et al. [19] have grafted fluorocarbon monomer onto a variety of surfaces by exposing them to a glow discharge.

(v) Mechanochemical grafting : The successive mechanical and ultrasonic shearing forces may also cause polymer degradation usually by a free radical mechanism. The mechanical degradation may be carried out by mastication, milling, high speed stirring or shaking. The thus generated free radicals in the presence of monomer initiate the grafting of latter onto the polymer surface.

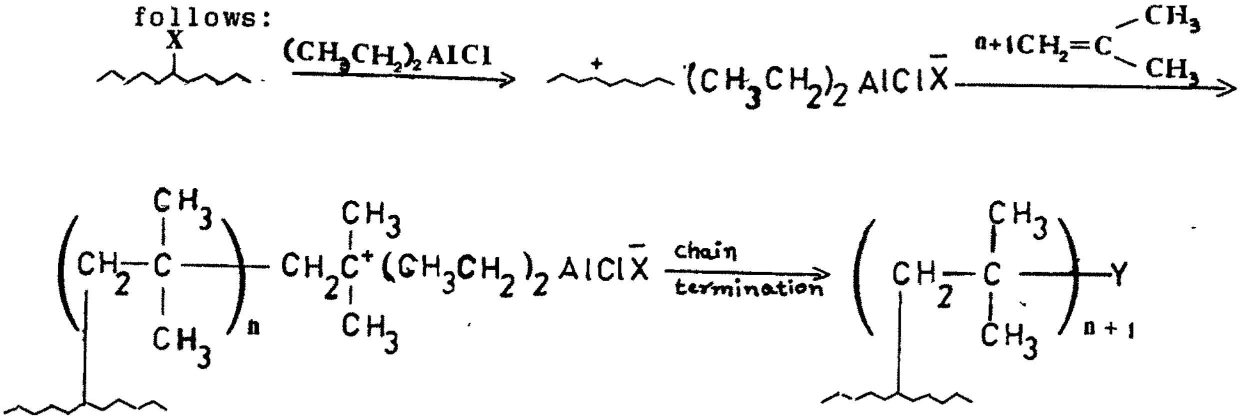
1.3.4.b Ionic mechanism

Graft copolymers are also formed through anionic or cationic polymerisation.

(i) Anionic method : Anionic polymerisation has become an excellent method for synthesis of block and graft copolymers. Graft copolymerisation is initiated by anions generated by the reaction of base with acidic protons in the main chain. e.g., polyamides [20,21], are metalated with sodium in liquid ammonia and then grafted with monomeric units.



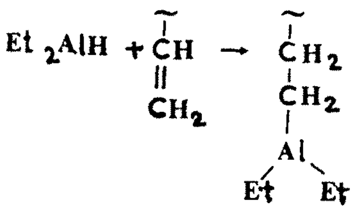
(ii) Cationic method : The initiation reaction between labile alkyl halides and lewis acids has been utilised for cationic grafting onto halogenated polymers [22] as follows:



1.3.4.c Coordination mechanism

Stereospecific initiators can give stereoblock copolymers which contain isotactic and heterotactic sequences. Greber [23] grafted olefins onto poly(Styrene-co-butadiene) using a

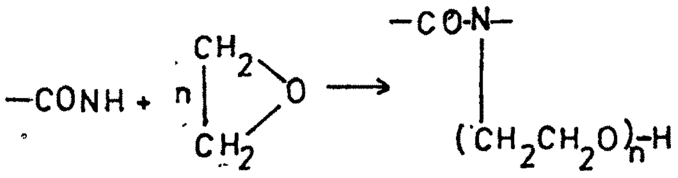
Ziegler-Natta coordination initiator system where diethyl aluminium hydride reacts with pendant groups to form a macromolecular trialkylaluminium.



Trialkylaluminium units with $TiCl_4$ or $TiCl_3$ form a Ziegler-Natta initiator system which is used in the grafting of α-olefins onto the preformed macro-molecular trialkylaluminium. By this technique, poly(styrene-co-butadiene)-g-ethylene or isotactic polypropylene was obtained.

1.3.4.d Coupling mechanism

Polymers containing active hydrogen are used for the synthesis of graft copolymers. Poly(ethylene oxide) is easily grafted onto nylon since the hydrogen atom of the amide nitrogen is readily removed.



Graft copolymers can also be prepared by coupling two or more polymers containing suitable functional groups.

1.4 REVIEW OF THE WORK DONE ON GRAFT COPOLYMERS OF PP

From the literature survey it is seen that the work carried out for the grafting of PP by free radical mechanism is mainly composed of photochemical and high energy radiation methods. However, as the proposed work is in free radical, chemical initiation process; only work done in this area is discussed below.

1.4.1 Free radical polymerisation (Chemical initiation)

Graft copolymerisation by chemical initiation mainly takes place through (a) chain transfer (b) hydroperoxidation and (c) halogenation. Hence the work done earlier is further classified in these subsections.

1.4.1.a Chain transfer

As mentioned in section 1.3.4.a (i), in order to produce a graft copolymer by a chain transfer mechanism, it is necessary to have three components in the system: a monomer to be polymerised, a polymer chain to be grafted, and a free radical initiator.

Canterino [27] grafted a mixture of acrylates on the polypropylene backbone using benzoyl peroxide initiator. A mixture of monomers containing benzoyl peroxide was spread on the polymer surface and heated to 70-80^{o}C producing a graft copolymer. Styrene, methyl methacrylate and diethyl methyl malonate were grafted on to PP [24] and mixture was degraded at 324^{o}C. Infrared analysis proved that the modified materials contained respective monomer unit on the PP surface. Vinyl pyridine, acrylonitrile and vinyl caprolactam were grafted onto PP fiber [25] by swelling the fiber in toluene containing 10 wt % benzoyl peroxide at 70°C. The tensile strength of the fiber was found to be unchanged after grafting but dyeing property was improved. Vinyl pyrrolidone was grafted for 3 h onto iPP [26] by dissolving iPP in xylene at 130°C in nitrogen atmosphere using free radical initiator. The grafted sample showed excellent dyeability. Vinyl pyridine was grafted onto PP fibers [28] by peroxidizing crystalline PP in an aqueous solution containing a non-ionic detergent and generating free radicals using benzoyl peroxide. The grafted fibers showed better dyeability. Nakatsuka et al. [29] stabilised PP by grafting it with glycidyl methacrylate. This grafted PP was milled with traces of 4-[3-(3,5-di-tert-butyl-4-hydroxphenyl) propionamido] phenol and a yarn spun at 270°C from this mixture was found to be stable for 54 h at 140°C, whereas unstabilized material (yarn) lasted only for 2 h.

Increased rate of grafting of methyl methacrylate onto PP [30] was found when PP was allowed to swell in n-heptane and treated with cumene hydroperoxide at 60°C. Wada et al. [31] carried out grafting of maleic anhydride onto PP at 120°C in the presence of benzoyl peroxide and found that the graft copolymer shows good bond strength to tinplate joints. Solution grafting of iPP [32] was carried out with acrylic acid in the presence of Bz_2O_2 at 140°C in o-dichloro benzene solvent. Highest grafting efficiency was observed for dilute solution of iPP and decreased melting point, heat of fusion and mol. wt. were observed for the products[33]. A reverse osmosis membrane with good salt retention was prepared from two phase PP [34] film containing grafted hydrophilic monomers. The grafted PP was prepared in solution at 120°C with acrylic acid, ethylene glycol methacrylate and arcrylamide and membranes were p~~o~~repared by solvent evaporation. Oomori and Iwata [35] prepared polypropylene-acrylic acid or methacrylic acid graft copolymer by dissolving PP in chlorobenzene and reacting the mixture of t-butyl peroxide and acrylic acid at 125°C for 6.5 h, with 10.5 wt % of acrylic acid. They found 2.2 wt % of acrylic acid in graft copolymer when p-xylene was used as solvent. Oomori [36] grafted N-butyl maleimide onto PP. The graft copolymer was prepared by dissolving PP in chlorobenzene at 125°C using dicumyl peroxide initiator for 3 h and obtained 89.5 : 10.5 PP-g-N-butyl maleimide. PP [37] was modified with bicyclo (2,2,1) hept-5-ene-2,3-dicarboxylic acid anhydride at 130°C in o-dichlorobenene using t-butyl peroxide initiator which gives 3 wt % of acid anhydride. Maleic anhydride was grafted onto PP [38] in the presence of Bz_2O_2 at 220°C and this grafted PP shows good adhesion for aluminium as well as nylon.

Vinyl trimethoxy silane was melt grafted onto iPP [39] using Bz_2O_2 as initiator at 210°C. This grafted PP was blended with iPP, the blend had HDT 180°C. In another patent [40] acrylic acid was grafted onto PP by heating PP, lauryl peroxide and 2,5-dimethyl-2,5-bis (t-butyl peroxy) hexane at 110°C for 1 h and then adding acrylic acid after lowering the temperature to 30°C. The grafted PP showed good adhesion to aluminium plates. Lokhande et al. [41] grafted methacrylic acid and acrylic acid onto PP fibers by emulsion polymerisation technique using benezoyl peroxide in benzene at 60°-80°C for 10 min- 8 h reaction time.

Graft polymers with good solubility are useful as emulsifier and were prepared by polymerisation of gaseous olefins and maleic anhydride onto PP [42] in chlorinated hydrocarbons using radical initiator at 80°C. Klosiewicz [43] synthesised graft copolymer by grafting butyl methacrylate onto PP in the presence of t-butyl peroxy benzoate at 135°C in chlorinated hydrocarbon solvent. The resultant graft copolymer had good adhesive property. PP was modified by heating PP powder with $CHCl_3$, acrylic acid and Bz_2O_2 initiator at 100°C for 10 min by Nemeck and Vesely [44]. Alkyl methacrylate-PP graft copolymers [45] were prepared by using t-butyl peroxy benzoate as an initiator. Whereas 4-methacryloxy propyltriethoxy silene was grafted onto PP powder [50] in an extruder at 160°C - 220°C using dicumyl peroxide initiator. Hope and Malley [46] synthesised olefinic polymer blend adhesive for bonding PP to polar substrates. These adhesives comprised PP grafted with unsaturated carboxylic acids or their derivatives. The rigidity, adhesion property and printability of PP were modified by grafting styrene onto PP.

The grafting was performed by suspending PP particles with vinyl monomers in aqueous medium [47] using t-butyl peroxy benzoate, 11.5 wt % of styrene was observed in grafted PP. The gas phase copolymerisation of styrene onto PP granuals [48] was carried out by using dicumyl peroxide initiator. The grafted sample had flexural modulus 17500 Kg/cm^2 compared with 14000 Kg/cm^2 of ungrafted PP. To improve graft level, toluene was used as an interfacial agent [49]. Toluene enhanced the grafting level significantly upto 12.5% at higher initiator concentration. The addition of toluene resulted in agglomeration in the final product due to uneven distribution in the reactor. Rangarajan et al. [51] grafted PP with maleic anhydride using Bz_2O_2 and novel catalyst RRKB-01 by solid phase polymerisation technique. The solid state N.M.R. analysis was performed to determine the presence of maleic anhydride. PP [52] was modified by mixing PP powder, maleic anhydride and Bz_2O_2 and using toluene as interfacial agent at 100°C. The grafting was observed to be only 0.26%.

Park et al. [53] carried out grafting of maleic anhydride onto PP in xylene with Bz_2O_2 initiator for 4 h at 120°C in nitrogen atmosphere and observed 3 % of maleic anhydride in grafted PP. Kai et al. [54] modified PP by mixing PP powder, maleic anhydride and benzoyl peroxide and heating this mixture for 3 h in autoclave at 100°C using 5 ml of toluene as interfacial agent. PP [55] was grafted with acrylonitrile and styrene in the presence of t-butyl peroxy pivalate by suspension polymerisation at 100°C. Mustonen et al. [56]

grafted itaconic acid onto PP by heating a mixture of PP powder and itaconic acid at $70^{0}C$ using dilauryl peroxide and 1,3-bis (t-butyl-peroxy isopropylene) benzene as initiator. Acrylamide polypropylene graft copolymer was prepared using inverse emulsion polymerisation technique [57]. The product was used as coupling agent for carbon fiber-reinforced PP composites. Furuta et al. [58] modified PP by heating mixture of PP, styrene, diallyl amine and t-butyl peroxy pivalate at $102^{0}C$ for 1 h. The grafted PP had surfacce resistance 2 x $10^{12}\Omega$. Yoshimura et al. [59] grafted glycidyl methacrylate onto PP using dicumyl peroxide at $200^{0}C$ by melt mixing technique. Hirose and Otsubo [60] prepared modified PP for tough moldings, by heating PP powder with Bz_2O_2 and styrene at $60^{0}C$ under nitrogen atmosphere for 1 h. This was followed by addition of talc and the mixture was heated upto $100^{0}C$ for 6 h.

1.4.1.b Hydroperoxidation

Hydroperoxidation has been extensively used for the graft copolymerisation of various vinylmonomers onto polypropylene. The hydrogen atom on the tertiary carbon atom is highly reactive with oxygen to form the hydroperoxide group which, upon decomposition, results in the formation of the free radical required for graft copolymerisation.

Natta et al. [61] carried out hydroperoxidation of PP without substantial degradation by heating in an air or oxygen current at $70-80^{0}C$. The hydroperoxidation was observed to be restricted to the surface or intercrystalline amorphous region. The hydroperoxidised PP was further used for the graft copolymerisation of methyl methacrylate, styrene and vinyl chloride. Wu et al. [62] grafted vinyl acetate onto hydro-peroxidised PP obtained by thermal oxidation in air. Minsker et al. [63] carried out oxidation of polypropylene at 70°C. The resulting hydroperoxidized polymer was used for grafting of methyl methacrylate using triethyl aluminium in n-heptane. Beati et al. [64] used t-butylperoxide as initiator during oxidation of PP and subsequently grafted 2-vinyl pyridine onto hydroperoxidised PP. A similar procedure was followed by Pegoraro et al. [65] for the grafting of methyl methacrylate.

Butadiene was grafted onto peroxidised PP [66] in the presence of ceric sulphate catalyst at 65°C for 48 h. The grafting was 5.9 % and Rockwell hardness of grafted PP was 87. Hydroperoxidation of PP in an aqueous slurry has been reported by Jabloner and Mumma [67]. A cationic surfactant and potassium persulfate were used to achieve wetting and initiate oxidation. Butadiene, vinylchloride and isoprene were grafted in the gaseous phase onto peroxidised PP surface [68]. The peroxidation of iPP was carried out by treating it with H_2O_2 in air at 10 atm for 35 h at 65°C. 2,3-Epoxy propyl methacrylate was grafted onto previously peroxidised iPP [69]. The PP was peroxidised by mixture of oxygen and ozone. The grafting was carried out in an aqueous emulsion containing 1:1 $FeSO_4$: EDTA disodium salt chelate as activator and Marsol as emulsifier. The maximum grafting was 16.7 %. Methyl methacrylate was grafted onto oxidised PP powder [70] in an aqueous emulsion containing $FeSO_4$, $7H_2O$ and tetramethylene tetraamine as activator in an inert atmosphere for 6 h at 30°C. Citovicky et al. [71] grafted water soluble vinyl monomers onto oxidised iPP powder at 30°C using emulsion polymerisation technique. Thermally peroxidised PP films were grafted with 2,2,6,6-tetramethyl piperidinyl methyl acrylate [72]. The light stability of grafted samples was found to be increased.

Ozonolysis has proved to be more effective technique for producing active sites on a polymeric backbone than air oxidation and offers a greater scope for graft copolymerisation of monomer onto PP.

Manasek et al. [73] grafted acrylonitrile onto ozonized PP in vapour phase. Many patents [74,75] are available where ozonized PP has been used for the preparation of graft copolymer of vinyl chloride and acrylamide. Patton [76,77] synthesised poly(propylene-g-2-vinyl pyridine) by selective hydroperoxidation of PP in aqueous slurry. A mixture of ozone-oxygen was bubbled at 60-100°C to introduce hydroperoxide groups. The product was then used for grafting of 2-vinyl pyridine in nitrogen atmosphere. Gawish [78] grafted styrene onto ozonized PP fiber. PP fibers were treated with ozone using oxygen as transporter at room temperature for 2 h. Then PP fibers were copolymerised with an aqueous emulsion of styrene.

Yamauchi and Yamaoka [79] carried out graft copolymerisation of methyl methacrylate onto ozone oxidised PP. They detected the active species in PP by ESR spectroscopy as a peroxy radical and found that total conversion and degree of grafting increased with ozone oxidation. Copolymerisation of methyl methacrylate onto ozone oxidised PP was also carried out by Matsui and Yamaoka [80]. They found higher degree of grafting for the vapour phase samples than for liquid phase samples.

4.1.1.c Halogenation

Halogenation offers another method to introduce functional groups in the polymer molecules. PP is an extremely unreactive nonpolar molecule. Hence, introduction of a chlorine atom into the polymer develops polarity in the molecule. Chlorination of PP generally involves heating of PP upto 60°C in a chlorinated hydrocarbon such as CCl_4. t-Butylperoxide and titanium tetrachloride were used as catalyst for chlorination [81,82]. Aoki [83] has studied various methods of chlorinating PP for its use in adhesives. Omichi et al. [84] have established a free radical mechanism taking place during chlorination of PP under γ-irradiation. The graft copolymerisation of styrene onto chlorinated PP has been carried out by Denes et al. [85]. Chlorination in CCl_4 has also been reported in the presence of UV light or natural light [86].

A summary of the work discussed is given in Table 1.1 for easy referencing.

1.5 PROPOSED WORK

From literature survey it has been observed that butyl acrylate and maleic anhydride have not been used systematically for the modification of polypropylene. It is also seen that the most of the work on PP grafting has been carried out by photochemical or high energy radiation activation methods. Very few references are available on the solution graft copolymerization technique. Grafting of PP by chemical initiation is restricted mainly to the surface grafting. As butyl acrylate has the lowest glass transition temperature (T_g) in the acrylate series ($-50^{0}C$), its incorporation into polypropylene as grafted chains is expected to result into a graft copolymer having lower Tg than that of other acrylates. On the other hand, maleic anhydride is very reactive and so higher percentage grafting and higher reactivity is expected on grafting of maleic anhydride onto PP.

Hence, we have attempted to synthesise the polypropylene-g-butyl acrylate and polypropylene-g-maleic anhydride by free radical initiation process. The experimental conditions are optimised and resulting products are characterised through various techniques. The graft copolymers have been further used as compatibilisers in the development of polypropylene/nylon-6 blends. The binary PP/Ny-6 and ternary PP/Ny-6/graft polymer blends with various compositions are prepared. The blends are characterised for mechanical, morphological and thermal properties.

Table 1.1

Survey of the work done on PP graft copolymer.

Sr. No.	Initiator used	Monomer used	Remarks	References
Chemical Initiation :				
1.	Bz_2O_2	Vinyl pyridine, acrylamide and vinyl caprolactam.	The PP fiber swollen in toluene and grafting was carried out at 70°C; increased dyeability.	25
2.	Bz_2O_2	Vinyl pyrrolidene.	Solution polymerisation; improved dyeability.	26
3.	Bz_2O_2	Mixture of acrylate.	Solution polymerisation.	27
4.	Bz_2O_2	Vinyl pyridine.	Increased dyeability.	28
5.	Bz_2O_2	Acrylic acid.	Solution graftng; highest grafting efficiency in dilute solution.	32
6.	Bz_2O_2	Glycidyel methacrylate.	Improved thermal stability.	29
7.	Bz_2O_2	Maleic anhydride.	Improved adhesive strength with tinplate joints and also with aluminium and nylon.	31, 38, 42
8.	Bz_2O_2	Acrylic acid, ethylene glycol methacrylate & acrylamide.	Solution polymerisation; membrane for reverse osmosis with good salt retention activity.	34
9.	Bz_2O_2	Maleic anhydride.	Solid phase graftion; toluene as interfacial agent.	49, 51, 54

10.	Bz_2O_2	Acrylic acid, methacrylic acid.	Emulsion Polymerisation	41,
11.	Bz_2O_2	Maleic anhydride.	Solution polymerisation.	53
12.	Bz_2O_2	Acrylamide.	Inverse emulsion polymerisation.	57
13.	Cumene hydroproxide	Methyl methacrylate.	Increased rate of grafting in n-heptane.	30
14.	t-Butyl peroxide	Acrylic acid.	Solution polymerisation.	35
15.	t-Butyl peroxide	Bicyclo[2,2,1] hept-5 ene-2,3-dicarboxylic acid anhydride.	Solution polymerisation.	37
16.	t-Butyl peroxide	2-Vinyl pyridine, methyl methacryalte.	Hydroperoxidation in air.	64, 65
17.	Dicumyl peroxide	Styrene	Vapour phase polymerisation Improved flexural strength.	48
18.	Dicumyl peroxide	N-butyl maleimide.	Solution polymerisation.	36
19.	t-Butyl peroxy benzoate	Butyl methacrylate. and Alkylmethacrylate.	Solution polymerisation; improved adhesion property.	43, 45
20.	t-Butyl peroxy benzoate	Styrene.	Improved rigidity, adhesion and printability. Suspension polymerisation.	47
21.	t-Butyl peroxy pivalate	Acrylonitrile, styrene.	Suspension polymerisation.	55

22.	Lauroyl peroxide	Acrylic acid.	Good adhesion with aluminium plate	40
23.	Oxygen	Methyl methacrylate, styrene, vinyl chloride and vinyl acetate.	Hydroperoxidation restricted to surface.	61, 62
24.	$K_2S_2O_8$	Methyl methacrylate.	Surface grafting.	67
25.	H_2O_2	Butadiene, Vinyl chloride, isoprene.	Vapour phase polymerisation.	68
26.	$FeSO_4$: EDTA disodium salt	2,3 epoxypropyl methacrylate.	16.7 % grafting	69
27.	Air oxidation	2,2,6,6-tetramethyl piperidinyl methacrylate.	Increased light stability.	72
28.	Ozone	Acrylonitrile.	Vapour phase grafting.	73
29.	Ozone-oxygen	2-vinyl pyridine.	Grafting was carried out in nitrogen atmosphere.	76, 77
30.	Ozone	Styrene	Emultion copolymerisation technique.	78
31.	Ozone	Methyl methacrylate.	Degree of grafting increased with ozone oxidation. Improved mechanical properties.	79, 80
32.	Titanium terachloride & t-butyl peroxide.	Vinyl monomers.	CCl_4 as medium for chlorination surface grafting.	81, 82
33.	UV & γ- radiation	Styrene	CCl_4 as medium for chlorination.	85, 86

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