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Graft Copolymerization of Vinyl Monomers onto Polypropylene

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INTRODUCTION

Modification of polymeric materials to improve their performance for specific use has been a fascinating field for research. A great amount of research work has been published in this area [1, 2]. Modification of polymers through graft copolymerization offers an effective means for introducing some desirable properties into the polymer without affecting the architecture of the polymer backbone.

Among synthetic polymers, polypropylene (PP) has occupied a prominent position because of its growing commercial application. However, this polymer has some drawbacks: it does not contain any reactive site, it has extremely poor hygroscopicity, it is difficult to dye, it has low melting and sticking temperatures, it is sensitive to photooxidation, and so on. This restricts its use in several technologically important fields. Hence, it needed some modification of its original properties before it could be used for a particular operation. Several methods are available for modifying polypropylene, of which graft copolymerization has proved an attractive means because the polymer not only retains most of its original properties but also acquires some additional properties needed for a particular application.

Polypropylene is 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

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hydrogen atom is involved in the degradation of a macromolecular chain. Hence, removal of this hydrogen atom by graft copolymerization with a wide variety of monomers provides a powerful method for partial modification of polypropylene and improves its thermal stability, photochemical stability, dyeability, mechanical properties, and softening temperature.

In the present review, graft copolymerization of polypropylene with vinyl monomers is discussed.

METHODS OF GRAFT COPOLYMERIZATION

The following three methods have been used for graft copolymerization onto polypropylene: chemical initiation, photochemical initiation, and high energy radiation-induced initiation.

Chemical Initiation

Graft copolymerization by chemical initiation may take place by any of the following methods.

Chain Transfer

In graft copolymerization by chemical initiation, monomer is polymerized in the presence of polymer. The initiation takes place by the decomposition of the added chemical initiator which abstracts hydrogen atom from the polymer chain to yield a free radical site for the polymerization of monomer. The initiation may also generate a free radical on a monomer unit. This growing polymer chain is terminated by the abstraction of a hydrogen atom from the polymeric backbone, leaving a free radical site.

Thus, 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 polymerized, a polymer chain to be grafted, and a free radical initiator. The efficiency of an initiator is an important factor in graft copolymerization. The free radicals obtained by the decomposition of the initiator must be capable of abstracting a hydrogen atom from the polymer surface to initiate polymerization of the monomer. Benzoyl peroxide [3-5], dicumyl peroxide [6, 7], and di-tertiary butyl peroxide [8] have been successfully used as initiators. A simplified kinetic scheme of graft copolymerization has been proposed by Natta et al. [9]. The step preceding grafting is the creation of an active center $\dot{S}$ on the polymeric chain (backbone):

$$\dot{X} + SH \longrightarrow XH + \dot{S} \qquad (1)$$

The radical $X^{\bullet}$ may be either a free radical ($R\dot{O}$) obtained from the decomposition of the initiator (R–O–O–R) or a radical consisting of an active monomer $M^{\bullet}$ or a homopolymer radical ($ROM_{n-1}M^{\bullet}$), later represented by $O^{\bullet}$ or a grafted radical ($S\text{-}M_{n-1}M^{\bullet}$):

$$R\text{–}O\text{–}O\text{–}R \longrightarrow 2RO^{\bullet} \tag{2}$$

$$RO^{\bullet} + nM \longrightarrow ROM_{n-1}M^{\bullet} \tag{3}$$

Step (1) is followed by a series of propagating reactions and by the termination reaction:

$$S^{\bullet} + nM \longrightarrow SM_n^{\bullet} \tag{4}$$

$$SM_n^{\bullet} + Y^{\bullet} \xrightarrow{kt} P \text{ or } 2P \tag{5}$$

In Step (5), radical $Y^{\bullet}$ may be whatever radical is present in the system (e.g., $RO^{\bullet}$, $\dot{O}$, $SM_{n-1}\dot{M}$). A grafted polymeric macroradical may also terminate by transfer with a substance T:

$$SM_n^{\bullet} + T \longrightarrow SM_n + T^{\bullet} \tag{6}$$

T may be homopolymer, the grafted polymer, the polymeric backbone SH, the monomer M, or the solvent.

The nature of monomer also plays an important role, and the success of the chain transfer method to produce graft copolymers depends upon the relative reactivity ratios in the copolymerization system. Canterino [10] grafted a mixture of acrylates on the polypropylene backbone. A mixture of monomers containing benzoyl peroxide was sprayed on the polymer surface and heated at 70-80°C to give a graft copolymer. Alternatively, polypropylene fibers have been heated in an initiator solution and the resulting polymer was soaked in styrene monomer to give grafted fibers [11].

A wide variation in temperature has been reported during grafting via the chain transfer process. Grafting of maleic anhydride has been carried out at 150°C [3], and styrene has been grafted at 60°C which is lower than the melting point of polypropylene [11]. Another patent [12] describes the graft copolymerization of styrene at a temperature above the melting point of polymer, but the temperature details are not given.

Natta et al. [9] carried out the graft copolymerization of methyl acrylate onto atactic polypropylene in the presence of various initiators; i.e., benzoyl peroxide, azoisobutyronitrile, lauroyl peroxide, and tert-butylperpivalate. The influence of different initiators and the concentration of monomer was studied. Surprisingly, the percentage of benzoyl peroxide initiator has been shown to have little influence on the content of methyl acrylate units present in the grafted polypropylene; the influence of various solvents on grafting was found to vary with the transfer constant of solvent-polymethyl acrylate radical. Interestingly, Oda et al. [13] have claimed in a patent the graft copolymerization of styrene and methyl methacrylate onto polypropylene in the presence of butylamine, pyridine, or formamide. An initiator was not used.

Introduction of Functional Groups into the Polymer

Graft copolymerization by the introduction of functional groups into the polymer has been an important method of modification. The polymer is reacted with chemicals to introduce functional groups along the length of the polymer chain to form reactive sites for grafting reactions. An essential feature of this type of grafting is that the initiation of polymerization occurs at these reactive sites only. The following methods have been used for introducing the functional groups into the polymer: hydroperoxidation and halogenation.

Hydroperoxidation. Hydroperoxidation has been extensively used for the graft copolymerization of various vinyl monomers onto polypropylene. A great deal of research work has been carried out by this technique [14-17]. The oxidation of polypropylene, as for most organic compounds, is an autocatalytic process [18-22], and controlled oxidation results in the formation of hydroperoxides [23-26]. The hydrogen atom on the tertiary carbon atom is highly reactive and hence is the site for reaction with oxygen to form the hydroperoxide group which, upon decomposition, results in the formation of the free radicals required for graft copolymerization. Chain scission is quite common in the polypropylene oxidation [27, 28], and it has been observed that the tertiary peroxy radicals are the intermediate precursors to scission [29].

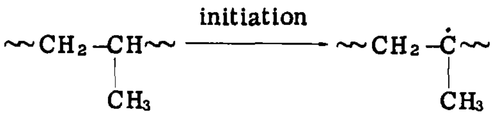
Natta et al. [30] carried out hydroperoxidation of polypropylene without substantial degradation by heating in an air or oxygen current at 70-80°C. The hydroperoxidation was observed to be restricted to the surface or intercrystalline amorphous regions. However, homogeneous peroxidation has been shown to occur during oxidation in solution in the presence of initiators. This hydroperoxidized polypropylene was used for the graft copolymerization of methyl methacrylate, styrene, and vinyl chloride monomers. Wu et al. [26] were able to graft copolymerize vinyl acetate onto hydroperoxidized polypropylene obtained by thermal oxidation in air. In another publication [31], the rate of formation of hydroperoxide groups in polypropylene by atmospheric oxidation was investigated. The influence of the number of hydroperoxide groups, temperature, time of reaction, and addition of ferrous sulfate during the grafting of acrylic acid was also investigated.

Minsker et al. [32] carried out the oxidation of polypropylene at

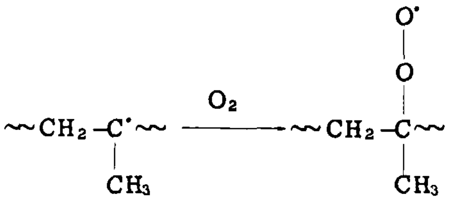
70°C. The resulting hydroperoxidized polymer was used for modification by graft copolymerization of methyl methacrylate monomer and by treating the polymer with triethylaluminum in n-heptane. It has been observed that the oxidation of polypropylene, initiated by initiators in a suitable solvent, has provided control over the extent of hydroperoxidation [33, 34].

Beati et al. [35] used tert-butyl peroxide as the initator during the oxidation of polypropylene and subsequently grafted 2-vinyl pyridine onto hydroperoxidized polypropylene. A similar procedure was followed by Pegoraro et al. [36] for the grafting of methyl acrylate onto polypropylene.

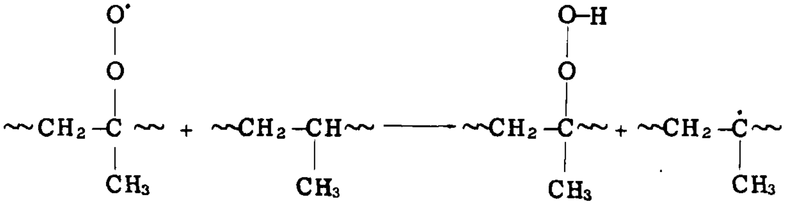
Hydroperoxidation of polypropylene in an aqueous slurry has been reported by Jabloner and Mumma [37]. A cationic surfactant and potassium persulfate were used to achieve wetting and initiate oxidation. Oxygen was sparged and heated to 100°C to get hydroperoxidized polypropylene. A surfactant has been shown to have a visible impact on hydroperoxide formation. Successful oxidation of polypropylene has been attributed to the formation of persulfate salt of the quaternary ammonium surfactant on the surface of the polypropylene. The subsequent thermal decomposition of this hydrophobic salt yields radicals, soluble in and reactive with the base polymer. The grafting of vinyl monomers onto polypropylene by free radical initiators has received much attention [38-41]. Uno et al. [42] synthesized graft copolymers from polypropylene hydroperoxide. Various methacrylic ester derivatives from glycidyl methacrylate and aromatic amines or phenols were synthesized. Graft copolymerization was carried out using benzoyl peroxide as initiator. The grafted fibers developed color when coupled with the aqueous benzene diazonium chloride solutions. Interestingly, the authors synthesized various azo dyes (polymerizable dyes) which have a double bond by reaction of methacrylic derivatives with diazonium salts and grafted onto polypropylene via the cleavage of a peroxide linkage.



$$\sim\sim CH_2-\underset{CH_3}{\underset{|}{CH}}\sim\sim \xrightarrow{\text{initiation}} \sim\sim CH_2-\underset{CH_3}{\underset{|}{\dot{C}}}\sim\sim \qquad (7)$$



$$\sim\sim CH_2-\underset{CH_3}{\underset{|}{C^{\bullet}}}\sim\sim \xrightarrow{O_2} \sim\sim CH_2-\overset{O^{\bullet}}{\overset{|}{\overset{O}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}}}\sim\sim \qquad (8)$$



$$\sim CH_2-\overset{\overset{O^\bullet}{|}}{\underset{\underset{CH_3}{|}}{\overset{\overset{O}{|}}{C}}}\sim + \sim CH_2-\underset{\underset{CH_3}{|}}{CH}\sim \longrightarrow \sim CH_2-\overset{\overset{O-H}{|}}{\underset{\underset{CH_3}{|}}{\overset{\overset{O}{|}}{C}}}\sim + \sim CH_2-\underset{\underset{CH_3}{|}}{\dot{C}}\sim \qquad (9)$$

$$\sim CH-\underset{\underset{CH_3}{|}}{\overset{\overset{O-OH}{|}}{C}}\sim \xrightarrow{\text{monomer}} \text{graft copolymer} \qquad (10)$$

Redox catalysts have been successfully used to prepare graft copolymers. Benzoin and ferric stearate or ferric acetylacetonate were used as redox catalysts to graft copolymerize N,N'-dimethylamino ethyl methacrylate and butyl acrylate onto hydroperoxidized polypropylene [37].

Ozonolysis has proved to be a more effective technique for producing active sites on a polymeric backbone than air oxidation and offers greater scope for graft copolymerization of monomers onto a polypropylene backbone. The extent and rapidity of grafting by this method suggests that other active species, such as peroxides and hydroperoxides, are formed.

Recently, Yamauchi et al. [43] studied the action of ozone on polypropylene. The formation of peroxy radicals on the polymer backbone was confirmed by electron spin resonance (ESR) spectra. A mechanism of oxidation has been proposed. Manasek et al. [44] were able to graft copolymerize acrylonitrile in the vapor phase onto ozonized polypropylene. Pavlinec et al. [45, 46] synthesized graft copolymer from hydroperoxidized polypropylene which was previously prepared by ozonization of the fibers. In another publication [47], styrene and methyl methacrylate were grafted onto peroxidized atactic polypropylene by using benzoyl peroxide and dicumyl peroxide as initiators. A detailed investigation of the effect of monomer concentration, type of initiator, temperature, and medium of reaction upon grafting efficiency was carried out. Among the solvents benzene, n-heptane, and n-butyl acetate, benzene was observed to have the highest grafting efficiency. More patents [48, 49] are available which used ozonized polypropylene for the preparation of graft copolymers of vinyl chloride and acrylamide.

Several authors [50-54] have used a mixture of ozone and oxygen to introduce functional groups into the polymer backbone. Patton [55, 56] synthesized poly(propylene-g-2-vinylpyridine) by selective hydroperoxidation of polypropylene in an aqueous slurry. A mixture of ozone-oxygen was bubbled at 65-100°C to introduce sufficient hydroperoxide groups. The product was then used for graft copolymerization of 2-vinylpyridine under a nitrogen atmosphere.

Halogenation. Halogenation offers another method to introduce functional groups into the polymer molecule [57]. Polypropylene is an extremely inactive nonpolar molecule because it lacks any reactive site. Hence, introduction of a chlorine atom into the polymer develops polarity in the molecule, and this polarity increases with an increase in the chlorine content of the polymer. Thus, activating the molecule for reaction with different chemicals may be used to initiate the graft copolymerization of various monomers.

Chlorination of polypropylene has been studied by a number of authors [58-60]. The most general method involves heating a polymer up to 60°C in a chlorinated hydrocarbon, generally carbon tetrachloride. t-Butyl hydroperoxide and titanium tetrachloride have been used as catalysts for chlorination [61, 62].

Aoki [63] has studied various methods of chlorinating polypropylene for use as an adhesive. Chlorination in carbon tetrachloride solution has also been reported by UV light or natural light [64-66]. Omichi et al. [67] have established the free radical mechanism occurring during chlorination of atactic polypropylene under γ-irradiation. Solid-state chlorination of polypropylene by ionizing radiation has been reported by Dzhagatspanyan et al. [68]. In another publication [69], these authors studied chlorination in a fluidized bed or in a water suspension by γ-irradiation in order to determine the change in crystallinity with an increase in chlorine content.

Ohshika [70] carried out the graft copolymerization of various vinyl monomers onto chlorinated polypropylene initiated by benzoyl peroxide and ultraviolet rays. The IR spectra of the copolymer obtained showed that acrylic acid, methyl methacrylate, acrylonitrile, and vinyl acetate were grafted onto polypropylene. Dehydrochlorination, dechlorination, and cross-linking were observed to take place during graft copolymerization. Recently, the graft copolymerization of styrene onto chlorinated polypropylene has been carried out by Denes et al. [71] by cationic mechanism.

Miscellaneous

Some other methods have also been applied for producing graft copolymers. When a polymer molecule is subjected to an applied shear or stress, bond scission may take place, producing free radicals at the ruptured ends of the chain. These sites may be used to initiate the graft copolymerization of monomers. The shearing forces used to produce free radicals include intensive shaking, high-speed stirring, and grinding. Czarczynska et al. [72] carried out the modification of polypropylene swollen in a 9:1 styrene-divinylbenzene solution by milling through a four roller calendar with the roll temperature increasing from 60-120°C. Grafting by milling has also been reported by others [73].

Terada [74] carried out the graft copolymerization of 1-phthalimido-1,3-butadiene by thermal mastication. The percentage of grafted monomer against feed was determined by UV spectroscopy.

Photochemical Initiation

Electromagnetic radiations in the visible and UV region have been widely used in the graft copolymerization of various monomers onto a polypropylene backbone [75, 76]. Exposure of a substrate to UV radiation results in excitation of the polymer molecule which can dissociate into reactive free radical sites on the polymeric backbone which can be used to initiate graft copolymerization.

Generally, some chemical substances are used as photosensitizers which act as the absorber of energy and transfer its energy to the polymer molecule present in the system, thus activating the molecule to give rise to sites for reaction. Among the most common sensitizers, benzophenone has been widely used [77-79]. Ang et al. [80] used biacetyl and benzoin ethyl ether in the photosensitized graft copolymerization of styrene, 4-vinylpyridine, and methyl methacrylate onto polypropylene. It was observed that styrene and 4-vinylpyridine give high graft yields owing to their ability to swell the polymer. Alternatively, polypropylene fibers may be treated with a solution of sensitizer which is absorbed on the surface of the fibers. These fibers, after irradiation with UV rays, may be grafted with acrylamide [81] or glycidyl methacrylate [82]. Recently, a similar procedure was used by Ogiwara et al [83]. Graft copolymerization of methyl methacrylate, methacrylic acid, and styrene has been carried out by coating different sensitizers, i.e., benzophenone, anthraquinone, and benzoyl peroxide, onto polypropylene film before exposure to UV radiation. Both vapor-phase and liquid-phase grafting has been carried out. The extent of grafting is reported to be as high as 700%. Seiber et al. [84] have reported the biacetyl-sensitized vapor-phase grafting of various monomers onto polypropylene fabric. The effect of wetting agents on grafting of methyl acrylate has been studied. It was found that polar hydrophilic solvents that do not wet polypropylene (water and n-propanol), and hydrocarbon solvents, such as benzene, give essentially no or very limited grafts, whereas polar solvents such as N,N'-dimethylformamide lead to extensive polymer grafting. Homopolymers are extremely less effective.

A recent investigation by Bellobono et al. [85] showed that graft copolymerization of an acrylate dye, 4-(N-ethyl, N-2-acryloxyethyl) amino, 4'-nitroazobenzene) onto polypropylene can be carried out by autosensitized photochemical initiation. A kinetic study was carried out to examine the characteristics of photochemical graft copolymerization. Two constant rate kinetics were observed. The authors suggest that the first constant rate is due to autosensitized hydrogen abstraction from the polymer surface by the dye, followed by the initiation of grafting of the monomeric or oligomeric species.

A brief induction period exists, after which the graft yield increases sharply with irradiation time. This autoacceleration phenomenon leads to a second constant rate, independent of the substrate. An explanation has been given on the basis of the fact that the original surface of polypropylene had been modified by the grafted dye, and this specific rate constant is due to the graft copolymerization of monomer onto the first grafted layer. Selli et al. [86] investigated the quantum yields as a function of wavelength during photochemical graft copolymerization of 4-(N-ethyl, N-2-acryloxyethyl) amino, 4'-nitroazobenzene monomer onto polypropylene fibers. Also, a kinetic approach of the process has been reported. A further kinetic investigation by Calgari et al. [87] was carried out to study the grafting of various acrylated azo dyes onto polypropylene in comparison with polycaprolactum and polyethylene terephthalate films. The effect of dye and the dye concentration upon grafting has been determined. An extrapolation of quantum yields has been made from Stern-Volmer plots.

Tazuke et al. [88] reported the photografting of acrylamide onto polypropylene film by using some sensitizers in an acetone reaction medium. The influence of sensitizers and additives has been investigated. Grafting has been confirmed to take place on the polymer surface only. The authors propose that graft copolymerization is initiated by abstraction of hydrogen from the polymer surface, caused by the triplet excited state of the sensitizer. A mechanism of photografting has been presented.

Graft copolymerization initiated by UV radiation of several monomers has been carried out on chlorinated polypropylene [70]. Another patent [89] describes a two-step process via hydroperoxidation for synthesizing the graft copolymers. Polypropylene was treated with 0.3% Ph_2CO in acetone and irradiated with ultraviolet light in the presence of air to get the hydroperoxidized polypropylene which was treated with a vinyl monomer, glycidyl methacrylate, in the presence of a reducing agent to give a graft copolymer.

High Energy Radiation Initiation

The radiation chemistry of polypropylene has been reported by a number of authors [90-96]. In recent years graft copolymerization by means of radiation has become a popular synthetic technique. Most of the recent literature on graft copolymerization describes the use of high energy radiation techniques [97-108]. The versatility of radiation initiation lies in the fact that such structural factors as number, length, and location of grafted chains can be controlled by careful selection of the dose and dose rate. Hence, it can be used to prepare any desired combination of polymers. An excellent study has been published by Chapiro [109].

In general, radiation grafting occurs whenever electromagnetic radiation passes through matter and its energy is dissipated by various physical mechanisms [110-113] i.e., photoelectric effect, Compton scattering, and production of electron pairs. However, two different processes result. One is the formation of ions and the other is the excitation of molecules. Once the ions and excited molecules are formed, they may undergo various secondary reactions including electron capture, charge neutralization, inter- and intramolecular energy transfer, and molecular dissociation to give free radicals, and these free radicals are the sole species for the initiation of polymerization. Precise knowledge of the nature of the radiation changes occurring in polypropylene and electron spin resonance (ESR) [114-128] of irradiated polypropylene strongly supports evidence that grafting is initiated by these free radicals only.

Numerous radiation methods have been developed for the preparation of graft copolymers. Among them, the following methods have been successfully applied to graft copolymerization onto polypropylene: direct radiation grafting, grafting onto radiation-peroxidized polypropylene, and grafting initiated by trapped radicals.

Direct Radiation Grafting

Direct radiation involves one of the simplest methods of synthesizing graft copolymers. The polymer is irradiated in the presence of monomer and in the absence of oxygen, which results in graft copolymerization of the monomer [129-130]. A considerable amount of work has been reported in the literature [131-140]. Since the action of ionizing radiation is unselective, all the components of a system are radiolyzed and have an impact on the mechanism of polymerization. Since radiation-induced grafting proceeds by the generation of free radicals on the polymer as well as on the monomer, the G value, i.e., free radical yield, expressed as the number of free radicals generated for 100 eV energy absorbed per gram, plays an important role in the grafting. Various aspects of direct radiation grafting have been investigated. A brief account is given below.

Swelling and thickness of film have been found to affect the degree of grafting considerably. Irradiation of polymer swelled in monomer gives some desirable results, and it has been observed that the grafting occurs all the way through the fiber. Since the monomer continuously diffuses into the swollen polymer, the yield of grafting reaches a higher extent. If the graft copolymerization exceeds the rate of diffusion of monomer into polymer, the reaction becomes diffusion controlled and strongly affects the overall kinetics.

Stamm et al. [141] showed that acrylonitrile and chloromethylstyrene penetrate the polymer easily and cause swelling of fibers without dissolving them. None of the monomers was found to cause detectable swelling at 25°C, but at higher temperatures the polymer showed marked swelling. The rate of grafting has been observed to decrease with an increase in film thickness [142]. It appears that the diffusion of monomer during the grafting process is affected by the film thickness. Simultaneously, the controlled diffusion of monomer into a polymer film or fiber will affect the thickness of the grafted area inside.

The number and the length of grafted branches formed in the direct method are determined by the dose and dose rate, respectively. The extent of grafting of ethyl vinyl ether onto polypropylene film has been reported to be directly proportional to the irradiation dose [143]. It was found that a linear relationship exists up to 30% grafting with no induction period at dose rates of 36.7, 49.4, and 70.6 rd/s. The dose rate dependence of the system was found to be 0.25. Stamm et al. [141] studied the grafting of chloromethylstyrene onto polypropylene at 25°C. The relation of the amount of monomer grafted to the total dose of irradiation was determined at dose rates of 0.4 and 0.03 Mrd/h. It was observed that all the points fall on one curve which shows a lack of dose rate dependence for the amount of monomer grafted provided the postirradiation time is long compared to the duration of the actual irradiation. Lee et al. [144] carried out the graft copolymerization of hydroxyethyl-methacrylate onto polypropylene and observed a linear relationship between extent of grafting and dose to a maximum value. A further increase in dose was found to result in graft degradation.

During the irradiation of polymer in liquid monomer, homopolymer formation largely results, thus considerably depressing the efficiency of monomer utilization. Therefore, the use of monomer vapor during graft copolymerization has attracted the attention of many researchers. This feature tends to avoid higher homopolymerization. A higher degree of grafting is sometimes attained with monomer vapor than with liquid monomer [145].

The selection of monomer also plays an important role in grafting. If the monomer itself is a good chain-transfer agent, numerous side chains are grafted onto the polymeric backbone. The length of the grafted chain will also be short.

A linear relationship is usually observed between the extent of grafting and postirradiation duration [142]. Studies by Stamm et al. [141] at two different temperatures showed that at 60°C the initial pick-up was higher compared to that at 25°C because of the higher rate of propagation at the former temperature. However, the percent pick-up with duration of postirradiation was found to be lower at higher temperatures. This has been attributed to an increase in the rate of radical termination.

The effect of irradiation temperature on the kinetics of graft copolymerization is very complex, and different results have been predicted. A change in temperature will strongly affect the kinetics of the grafting reaction. One of the factors, the viscosity of the medium, is reduced with the increase in the temperature of graft copolymerization, and hence have a direct impact on the gel effect. Furuhashi et al. [145] observed that the grafting rate increases with an increasing irradiation temperature, attaining a maximum value at 50-60°C. A further increase in temperature resulted in a decrease in rate. This has been attributed to an increasing rate of chain termination at higher temperature.

It has been observed that a marked accelerative effect on the rate of grafting arises when a proper solvent is used along with a monomer. In general, a good solvent may act as a swelling agent and hence will favor the diffusion of monomer into the polymer. Methanol has been reported to show an accelerating effect on the overall rate of grafting [142]. Odian et al. [146-148] investigated the accelerating effect of methanol on radiation-induced grafting of styrene and acrylates on polypropylene. The increased rate of grafting upon dilution of styrene with methanol was attributed to the onset of the "Trommsdorff effect" which arises due to the insolubility of the growing graft polystyrene chains in methanol.

Burchill et al. [149] reported the accelerating effect of various solvents on the rate of grafting. It was found that methanol increases the rate of grafting, but no accelerating effect was observed when benzene was the diluent. However, a methanol-benzene mixture was observed to have a pronounced maximum at benzene concentrations up to 10%. A similar effect was observed when benzene was replaced by hexane which, like benzene, swells the polymer. The accelerating effect in methanol-benzene and methanol-hexane has been attributed to swelling of polypropylene and to entanglement of the grafted polymer chain which reduces the rate of termination but not the rate of propagation.

Grafting onto Radiation Peroxidized Polypropylene

Investigation of the graft copolymerization of vinyl monomers onto polypropylene preirradiated in air has been extensively studied [150-153]. When polypropylene is subjected to high energy radiation in air, macromolecular peroxides and hydroperoxides are formed [154, 155] which, upon decomposition in the presence of monomer, initiate the copolymerization of monomer, forming a graft copolymer. Irradiation of polypropylene in air has been carried out by a number of workers [156-158]. Decker et al. [159] studied the rate and oxidation products during the γ-initiated oxidation of polypropylene. However, a prolonged exposure of polypropylene to γ-rays in oxygen may result in a number of products instead of polymeric hydroperoxide [160-163].

The mechanism of peroxidation in polypropylene has been studied in detail by Chapiro [164]. He recently investigated [165] the graft copolymerization of acrylonitrile onto peroxidized polypropylene. The kinetics and mechanism of radiation peroxidation were also investigated. Various steps usually involved in peroxidation are the same as mentioned earlier under chemical initiation, according to which polymeric hydroperoxides (POOH) arise as a result of a chain reaction (Eqs. 7-9). However, cross-linking is quite common in radiation peroxidation. Diperoxides (POOP) or peroxidic cross-links are formed by the combination of two polymeric radicals:

$$\mathrm{POO^{\bullet} + P^{\bullet} \longrightarrow POOP} \qquad (11)$$

$$\mathrm{POO^{\bullet} + POO^{\bullet} \longrightarrow POOP + O_2} \qquad (12)$$

where P represents the polymer. When such polymeric peroxides are used to initiate a graft copolymerization reaction, diperoxides generate only graft copolymer while hydroperoxides lead to equivalent amounts of graft copolymer and homopolymer. The thermal decomposition of the diperoxide produces PO$^{\bullet}$ radicals while hydroperoxide produces PO$^{\bullet}$ and OH$^{\bullet}$ radicals:

$$\mathrm{POOP \longrightarrow 2PO^{\bullet}} \qquad (13)$$

$$\mathrm{POOH \longrightarrow PO^{\bullet} + {}^{\bullet}OH} \qquad (14)$$

These radicals, formed by thermal decomposition, initiate graft copolymerization and homopolymerization.

Initiation:

$$\mathrm{PO^{\bullet} + M \longrightarrow POM^{\bullet}} \qquad (15)$$

$$\mathrm{OH^{\bullet} + M \longrightarrow OHM^{\bullet}} \qquad (16)$$

Propagation stage:

$$\mathrm{POM^{\bullet} + nM \longrightarrow POM^{\bullet}_{n+1}} \qquad (17)$$

$$\mathrm{\dot{O}HM + mM \longrightarrow OHM^{\bullet}_{m+1}} \qquad (18)$$

Termination stage:

$$\mathrm{POM_n^{\bullet} + POM_m^{\bullet} \longrightarrow} \text{ grafted and cross-linked polymer} \qquad (19)$$

$$\mathrm{POM_n^{\bullet} + OHM_m^{\bullet} \longrightarrow} \text{ grafted polymer} \qquad (20)$$

$$\mathrm{OH\,M_n^{\bullet} + OHM_m^{\bullet} \longrightarrow} \text{ homopolymer} \qquad (21)$$

Chain termination may take place to either the monomer or another polymeric chain:

$$POM_n^{\bullet} + P \longrightarrow POM_n + P^{\bullet} \tag{22}$$

$$POM_n^{\bullet} + M \longrightarrow POM_n + M^{\bullet} \tag{23}$$

A wide variety of monomers has been grafted onto polypropylene. It has been observed that graft copolymerization is influenced by a number of factors such as dose, dose rate of irradiation, film thickness, monomer concentration, temperature, solvent used, and added substances.

The radiation dose has been observed to show a marked effect on the accumulation of hydroperoxides. At low doses the concentration of peroxides in the polymer has been found to increase with an increase in dose. Since the number of grafted branches is directly proportional to the number of peroxidic sites, grafting will increase with the preirradiation dose (Fig. 1). Because the peroxides initiate the polymerization of monomer upon decomposition, the number of sites will also be responsible for the length of the grafted branches. Sobue et al. [158] studied the influence of dosage upon grafting at particular preirradiation intensities. The rate of grafting was found to be proportional to about the 3.4 power of dosage at 135°C. The

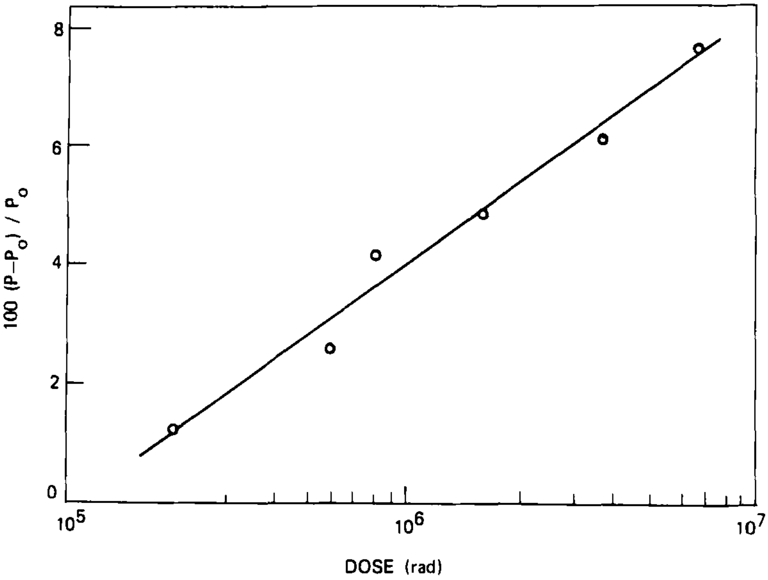


FIG. 1. Effect of irradiation dose on the percentage of grafting of vinyl chloride. Vinyl chloride, 760 mmHg; reaction time, 3 h; reaction temperature, 0°C; irradiation temperature, -78°C [166].

results confirm that a chain reaction occurs in the formation of the hydroperoxides. Chapiro [164] studied the graft copolymerization of acrylonitrile onto polypropylene film preirradiated at various doses in air. It was observed that for low doses the conversion curves exhibit an autocatalytic character, typical of the gel effect, but at very high doses the curves have been observed to level off after a critical grafting ratio is reached and then drop with any further increase in the preirradiation dose.

The rate of grafting is influenced by the dose rate of preirradiation. It has been observed that low dose rates give favorable results. At a fixed dose, the rate of grafting is faster with a low dose. Sobue et al. [167] mentioned the same trend and explained that at a higher dose rate the recombination of the two polymeric radicals is higher and diffusion of oxygen into the polymer film was a rate-determining factor. O'Neill [168] reported that in the latter stages of the reaction, the overall rate of grafting increases as the dose rate is decreased.

During irradiation of polymeric radicals, there is competition between the reaction with oxygen and self-combination, resulting in cross-linking. In the easily accessible region of a polymeric matrix, there is no oxygen diffusion control. Hence, oxygen scavenges all polymeric radicals to the detriment of the competing cross-linking process. Within the unaccessible region of a polymer, peroxidation may easily be under oxygen diffusion control. Hence, at very high dose rates the irradiation period is very short. The peroxide concentration built up per unit dose decreases with an increase in dose rate as a consequence of competition from the cross-linking radical-combination reaction.

When irradiated polypropylene fibers are kept for several hours at room temperature, they are still capable of initiating graft copolymerization. It has been observed that the degree of grafting decreases with the storage time, which must be due to a drop in peroxide concentration. Eda et al. [126] studied the preirradiation of polypropylene in oxygen. Studies on the isothermal decay of peroxyradicals at 40°C showed that the high initial rate of decay is followed by slow decay. Sundardi et al. [169] have shown that the concentration of polypropylene hydroperoxide decreases with time due to deactivation of polymer chains by decomposition of hydroperoxide. This effect has been found to be more pronounced at higher temperatures.

It has been seen that the grafting rate increases with the time of reaction. Sobue et al. [167] found that there is a linear increase in grafting rate up to 60 min during the grafting of acrylonitrile onto polypropylene film, but no indication of saturation was observed. Chung et al. [170] reported that the degree of grafting increases linearly with increasing time. Sundardi et al. [169] observed that the degree of grafting with time reaches a maximum after 2-3 h. Temperature was also found to have a large impact on the rate. This can be understood from the observation that the maximum grafting at 50°C was 18% which reached 28 and 42% when the temperature was raised to 60 and 70°C, respectively.

Many substances present even in very small amounts can strongly affect the kinetic parameters of radiation grafting. Thus, if any added substance has a high chain transfer constant, the overall yield of grafting may be reduced due to chain transfer of the growing chain to the added substance. Torikai et al. [171, 172] reported that grafting is remarkably accelerated by H_2O addition. Minnema and Hazenberg [173] studied the grafting of vinyl monomers onto hydroperoxidized polypropylene in redox systems. Three systems studied were ferric acetylacetonate plus benzoin, ferrous acetylacetonate plus benzoin, and cobaltous acetylacetonate. These accelerators diffuse into the polymer film along with monomer and cause a considerable increase in the rate of grafting. This enhancement is highly marked at lower temperatures.

During graft copolymerization, homopolymer is also formed. It has been predicted that the mobile $^{\bullet}OH$ radical formed during the thermal decomposition of hydroperoxide is responsible for the polymerization of monomer into the homopolymer. Homopolymerization may further arise during the grafting process by the dissociation of low molecular weight peroxides, hydroperoxides, or hydrogen peroxide (H_2O_2) which may be present in the irradiated polymer. Some authors have used a reducing agent to overcome this problem, thus decomposing the peroxy radicals and converting $^{\bullet}OH$ to the inactive OH^- ion. Ferrous ions have been most commonly used to reduce homopolymerization during grafting [174]. O'Neill [168] investigated the influence of ferrous ion concentration on the grafting rate. It was observed that reaction rate initially increases with increasing $[Fe^{2+}]$. Somewhere in the range $3.6 \times 10^{-4} < [Fe^{2+}] < 7.9 \times 10^{-4}$ molal, a maximum rate is attained and thereafter the effect of increasing $[Fe^{2+}]$ retards the process. The following steps have been mentioned:

Peroxide decomposition:

$$POOH + Fe^{2+} \xrightarrow{K_1} PO^{\bullet} + OH^- + Fe^{3+} \tag{24}$$

Radical scavenging:

$$PO^{\bullet} + Fe^{2+} \xrightarrow{K_2} PO^- + Fe^{3+} \tag{25}$$

Chain initiation:

$$PO^{\bullet} + M \xrightarrow{K_3} PO\text{–}M^{\bullet} \tag{26}$$

where POOH and M represent the polymeric peroxy species and the monomer, respectively. At higher molal concentrations, the rate of grafting decreases. O'Neill explained that the competition of the $PO^{\bullet}$

radical between Fe^{+2} and M is determined by the instantaneous value of $K_2[Fe^{2+}]/K_3[M]$ which is much higher within the peroxidized polymer film than in the external medium and/or $K_2 \gg K_3$. Thus, an increase in $[Fe^{2+}]$ must at some point result in predominance of the radical "wasting" reaction according to Eq. (25), hence reducing the overall rate of grafting.

Matsuda et al. [175] carried out the irradiation of polypropylene at Dry Ice temperature in the presence of air. The peroxide radicals thus produced were able to initiate very efficient graft copolymerization with a rise in the reaction temperature. Thus homopolymer formation due to heating and to hydroxyl radicals from the cleavage of hydroperoxide was depressed to a great extent. Various solvents added to the reaction system also influence the kinetics of grafting [176].

Grafting Initiated by Trapped Radicals

When a polymer is subjected to ionizing radiation in the absence of oxygen, trapped free radicals are formed. These radicals have been found to remain active for a long period and are capable of initiating further graft copolymerization whenever they are brought into contact with the monomer. The versatility of this method lies in the fact that the extent of homopolymerization is very small because the monomer is not exposed to radiation. The temperature required for the grafting reaction is also much lower. Although the method has been successfully used for grafting various vinyl monomers onto polypropylene [177-182], the grafting yield obtained by this method will depend directly on the efficiency of radical trapping. High radiation doses are required to bring about reasonable amounts of polymer grafting because, following irradiation, the number of free radicals decreases with time [127] owing to chain termination and radical recombination. Hence, it is necessary to use the trapped radicals immediately after irradiation and to carry out the radiation at low temperatures. Graft copolymerization has been found to be influenced by dose, dose rate, grafting temperature, etc.

Sundardi [169] investigated the graft copolymerization of vinyl pyrrolidone and acrylic acid by the trapped-radical initiation method. The degree of grafting was found to be directly proportional to the log of the irradiation dose. The results appear to be in good agreement with the kinetics of graft copolymerization initiated by trapped radicals. For a low dose of irradiation it can be assumed that the concentration of trapped radicals is proportional to the irradiation dose. At a constant irradiation dose, the degree of grafting has been found to increase almost linearly with reaction time. The influence of temperature upon grafting has been studied over a wide range. With an increase in reaction temperature, the degree of grafting has been found to increase, reaching a maximum value at 70°C and then tending to decrease with a further rise in temperature (Fig. 2). This relationship between the rate of grafting and temperature has been

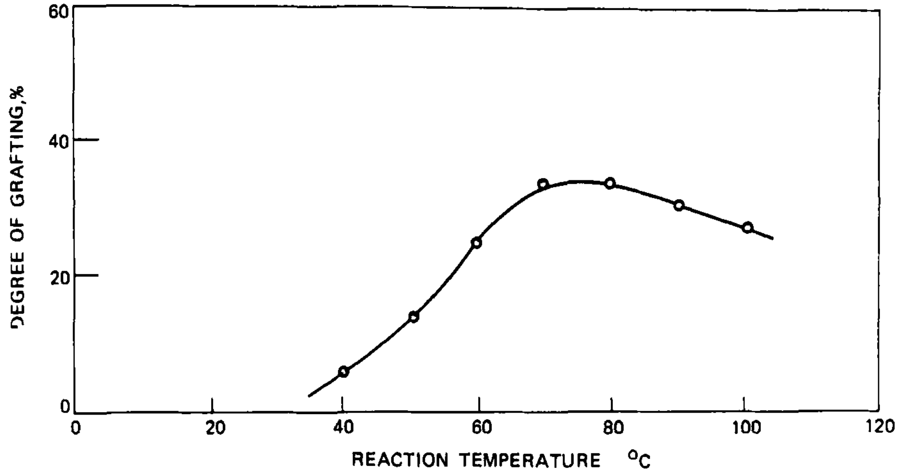


FIG. 2. Influence of reaction temperature on the degree of grafting of PP fibers. Grafting reaction with 1-vinyl-2-pyrrolidone monomer in pure condition. Dose of r-irradiation, 1.92 Mrd [169].

explained on the basis of the fact that the rate of radical termination by combination also increases at higher temperature, creating competition between chain propagation and chain termination. Hence, due to the higher rate of radical combination at higher temperature, the number of free radicals available for grafting is decreased, resulting in an overall decrease of degree of grafting.

Addition of some substances has been found to increase the rate of grafting. Natural salts (Na_2SO_4) and surface-active agents (Emaru 40) accelerate grafting to some extent [183]. Iwakura et al. [184] have shown that addition of C_6H_6 to monomer greatly increases the rate. The initial rate is slow with acetone.

SEPARATION AND CHARACTERIZATION OF PURE GRAFTS

The separation of homopolymer formed during grafting is done by Soxhlet extraction with a suitable solvent, leaving behind copolymer only. Fractional precipitation has been used to isolate fractions of polymers of varying molecular weights, followed by intrinsic viscosity $[\eta]$ and gel-permeation chromatography (GPC) to determine the molecular weight of poly(propylene-g-dimethyl amino ethyl methacrylate) [37].

Microinterferometry has been applied as a quantitative method for determining the transversal distribution of graft concentration instead of the usual determination of an overall graft concentration of the radiation-induced polypropylene graft copolymers [142, 145]. The pure graft copolymer is further characterized by spectroscopic examinations such as infrared spectroscopy, nuclear magnetic resonance, and x-ray. Ultraviolet spectroscopy gives an estimate of the percentage of grafted monomer versus the feed [74].

APPLICATIONS

The chemical modification of polypropylene by graft copolymerization has been carried out to impart some desirable properties to the polymer for its use in particular applications. The extent of grafting and its distribution along the polymer has a large impact upon its ability for use in a particular operation. As a result of grafting, major achievements have been reported in dyeability, thermal stability, mechanical properties, and composites.

Dyeability

To make polypropylene more dyeable, a number of efforts have been made [81, 134, 185, 189]. Various hydrophilic monomers have been grafted onto polypropylene in order to increase its dyeability. Uno et al. [42] carried out the graft copolymerization of glycidyl methacrylate and its derivatives. These were later coupled with diazonium salts. Interestingly, azo dyes were grafted onto polypropylene fibers. The colors developed ranged from yellow to violet.

Sundardi [169] has published an excellent work on graft copolymerization of such vinyl monomers as vinyl pyrrolidone, acrylic acid, acrylonitrile, and acrylamide. It was observed that grafted fibers can be dyed with almost all kinds of dyes, including direct, naphthol, disperse, reactive, basic, acidic, and vat dyes.

The results show that among the vinyl monomers studied, vinyl pyrrolidone seems to be the best monomer. It gives excellent dyeing properties with such dyes as basic, acidic, disperse, and napththols. Washfastness for polypropylene fibers grafted with vinyl pyrrolidone was also found to be fairly good.

Moisture Absorption and Antistatic Properties

The unmodified fibers of polypropylene have a slippery and cold feeling. The moisture absorption of polypropylene fibers is almost negligible. Therefore, the fabric made from these fibers has a very

TABLE 1. Antistatic Ratings of CMS-Grafted Polypropylene Fibers [141]

No.	Treatment	Antistatic rating 1-5 scale, 1 is best
1	Polypropylene with no modification and no additives	5
2	Reevan 3 denier tow, as received	2
3	(2) Treated with DMF at 120°C, 1 h	3
4	(2) With 19.4% CMS graft, dyed in DMF 120°C, 1 h	3-4
5	(2) With 8.3% graft, pyridine treated	2
6	(5) Dyed in aq bath, 100°C, 1 h	2

low antistatic behavior. Stamm et al. [141] carried out the grafting of chloromethylstyrene (CMS) onto polypropylene fibers and noted that grafted fibers, when heated with pyridine, showed a marked improvement in antistatic properties. Modified polypropylene fibers with 10% CMS-graft and pyridine treated had a moisture regain of 3.88%. The antistatic rating of CMS-grafted PP fibers is shown in Table 1.

As a result of grafting of hydrophilic monomers, the moisture regain of the fibers increases [190] and depends upon the degree of grafting. Vinyl pyrrolidone and acrylic acid have proved to be the most excellent monomers for improvement of the moisture absorption property of polypropylene fibers (Table 2). A linear relationship between moisture regain and degree of grafting is shown in Fig. 3.

Thermal Properties

Polypropylene has a sticking temperature (140°C) and melting temperature (167°C) which limit its use in operations conducted at higher temperatures. Hence, improvement in the thermal stability of polypropylene has made its use possible at higher temperatures. Table 2 shows the increase in melting point with the degree of grafting for all the fibers. Vinyl pyrrolidone and acrylic acid monomers have proved to be most excellent monomers for improvement of melting behavior up to 300°C. The sticking temperature has also been shown to increase considerably when chloromethylstyrene has been grafted onto polypropylene. Lodesova et al. [101] have shown that following the grafting of acrylonitrile and glycol methacrylate

TABLE 2. Melting Point and Moisture Regain of Grafted Fibers [169]

Grafted fibers	Degree of grafting (%)	Melting point (°C)	Moisture regain, % at relative humidity 65%
PPVP[a]	12.0	230	1.5
	13.9	233	2.1
	16.8	>300	2.5
	27.8	>300	4.2
PPAN[b]	1.4	164.1	0.20
	6.9	193.7	0.43
	10.4	197.4	0.32
	14.1	211.6	0.33
	25.8	217.6	0.26
PPAM[c]	1.2	162.7	3.17
	2.6	163.7	3.01
	3.6	166.6	2.17
	7.1	167.0	1.99
	13.4	169.3	2.60
PPAA[d]	12.1	223.0	0.70
	18.8	>300.0	1.60
	25.5	>300.0	2.50
PP	0.0	163.0	0.00

[a] PP fibers grafted with vinyl pyrrolidone monomer.
[b] PP fibers grafted with acrylonitrile monomer.
[c] PP fibers grafted with acrylamide monomer.
[d] PP fibers grafted with acrylic acid monomer.

monomers, the melting behavior of polypropylene fibers is considerably increased. The thermal decomposition temperature of both copolymers has been reported to be in the range 298-423°C.

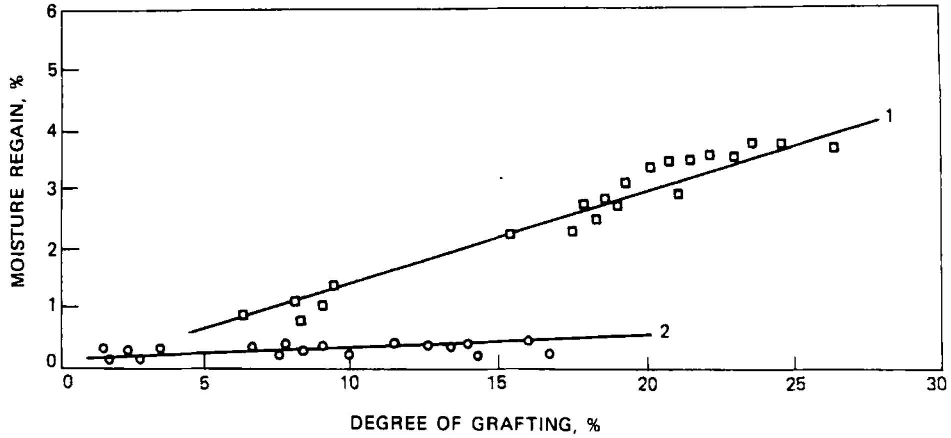


FIG. 3. Influence of the degree of grafting on the moisture regain of PP grafted fibers, measured at 65% RH and 25°C; (□) PPVP, (○) PPAN [169].

Composites

One of the most important applications of polypropylene is in the formation of composites. This has attracted the attention of several authors recently [191]. Sasaki et al. [192] investigated the mechanism for reinforcement with glass fiber in polypropylene grafted with acrylic acid. The grafted polypropylene exhibits good adhesion to glass fiber coupled with aminosilane or epoxysilane to improve the mechanical strength and heat resistance. Uniformity of fiber dispersion also increases with decreasing melt viscosity of grafted polypropylene. Sasaki et al. claimed [193] that the mechanical properties and the heat resistance of glass fiber-reinforced polypropylene are improved markedly by grafting with a small amount of acrylic acid or maleic anhydride.

One of the most important factors for reinforcement is adhesion. Recent efforts have also been made by various workers to improve the adhesion property of the polymer [178, 194-198]. The grafting of maleic anhydride onto polypropylene has been observed to result in a modified polymer with high tearing adhesive strength [3, 199, 200]. A recent patent [201] indicates that the glass-reinforced polypropylene sheet prepared from maleic anhydride grafted onto polypropylene has a tensile strength of 1130 kg/cm^2 and an Izod impact strength of 60 kg·cm/cm.

Fiber-reinforced composite membranes with high mechanical and chemical strength have been successfully prepared [202, 203]. Gehringer et al. [204] grafted mixtures of acrylic acid and ethyl acrylate, 2-hydroxyethyl acrylate, or butyl acrylate onto polypropylene films under an electron beam. The films were pressed against aluminum to prepare composites. Tensile strength improvement of short graphite fiber-reinforced polypropylene has also been reported by grafting [191].

Miscellaneous

Among several other applications, grafting of acrylic acid onto polypropylene has been used to produce a semipermeable membrane [205-207]. Ion-exchange membranes have been synthesized by grafting phosphoric acid onto polypropylene [72, 208]. Ito et al. [209] carried out the grafting of PP film to introduce some ligand groups. This film was used to detect heavy metal ions in water, which gives a color reaction with the ligands in the membrane. Chloromethylstyrene has been grafted onto polypropylene and bonded to metalloporphyrins for its use as a catalyst in oxidation reactions [210].

Graft copolymers of polypropylene have recently occupied a prominent position in the biochemical field and have been successfully used for the surface modification of vascular prosthesis made from PP films [211]. Other applications of graft copolymers are in blood compatibility and in recalcification time.

The tensile properties of polypropylene have been improved by grafting various vinyl monomers [212-215]. One of the important approaches of graft copolymerization is the inclusion of flame retardancy in surface grafts. Vinyl monomers containing phosphorous have shown good flameproofing properties when grafted to polypropylene [216].

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