

Review

Improvement of Polypropylene Properties by Irradiation/Grafting and Other Modifications

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POLYPROPYLENE (PP) is a cheap fabric, bearing chemical resistance and excellent mechanical properties. PP is hydrophobic in nature, inactive synthetic fabric due to the absence of reactive functional groups in the molecular structure, thus preventing its dyeing. For this reason, PP fibers are modified by irradiation methods to form free radical centers onto the surface and graft copolymerization of selected vinyl monomers. Different irradiation techniques are adopted involving plasma discharge, electron beams, ozone, UV, γ - rays and others.

PP is grafted with selected monomers including methacrylate derivatives such as (2N -Dimethyl amino ethyl methacrylate, 2N morpholino ethyl methacrylate, 2- ethyl methacrylate phosphoric acid, methyl methacrylate, 2- hydroxy ethyl methacrylate) acrylic acid, styrene, chloro methyl styrene, vinyl acetate etc...

The different variable factors affecting irradiation and grafting reactions are considered such as irradiation dose, storage time of irradiated fabric, monomer concentration, reaction time and temperature. Physical properties of grafted and those containing tertiary amino quaternized groups are improved for increase of moisture regain, melting point and enhancement affinity to dyeing by different classes of dyestuffs. The important properties improvement include ion exchange capacity, electrical conductivity, antistatic, insect repellent activity antibacterial property. PP containing Ag, Zn, ZnO, TiO₂, Cu, Cu₂O nano particles are antibacterial fabrics which are used as wound healing dressings.

Keywords: Polypropylene, Irradiation, Grafting, Dyeing, Antistatic antibacterial, Insect repellent and ion-exchanger properties.

Introduction

PP macromolecule chains are represented as follows:

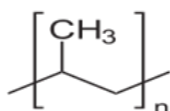


Fig. 1. Chemical structure of Polypropylene.

Polypropylene (PP) has excellent mechanical properties and chemical resistance and is inexpensive compared to other synthetic fibers. In addition, PP fibers have many important applications[1] for filtration, packaging purposes, disposable and non disposable medical products, upholstery, carpets, blankets, apparel fabrics (sweaters), sport, swim and underwears), military uniforms automotive lining fabrics, ropes, wire cable coating, geo-textiles for road construction, drainage, coastal and river bank protection. PP is used in different hygienic and medical application such as surgical masks, diapers burns, wound

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healing dressings and hygiene bands.

The disadvantages of PP fibers are poor hydrophilic, paraffinic feel and high crystallinity. These fibers bear no reactive functional groups and have no affinity for normal dyestuffs. In order to improve these properties, PP fibers are modified by various techniques to allow easy dyeing.

Modifications of PP process comprises activation and formation of active sites onto the main macromolecules of PP chains using different radiation processes or other means, followed by reaction of selected monomers on the formed sites by chain polymerization reaction mechanism which are represented by the following:

- 1- Initiation (formation of active sites).
- 2- Propagation (growth).
- 3-Termination.

Irradiation and Grafting of polypropylene

Graft copolymerization of selected vinyl monomers onto PP activated chains is an important method for PP modification. Different methods

for PP initiation involve the following steps:

- 1- Plasma discharge
- 2- Ionizing radiation by electron beam, UV radiation, ozone treatment, photo-initiation and gamma rays.
- 3- Chemical initiation by a redox system such as azo-initiation.

Plasma discharge

Plasma discharge device is an eco- friendly, dry process, which is usually used for activation of polymers without affecting the bulk properties[2] and has the advantage to minimize water, energy and chemicals consumption. Atmospheric pressure plasma (corona discharge) and low pressure plasma (glow discharge) are well known popular techniques. During plasma discharge, the electrons acquire their kinetic energy from the applied voltage. Plasma discharge exposure to fabric and then grafting results in excellent hydrophilic, wettability and dyeing properties.

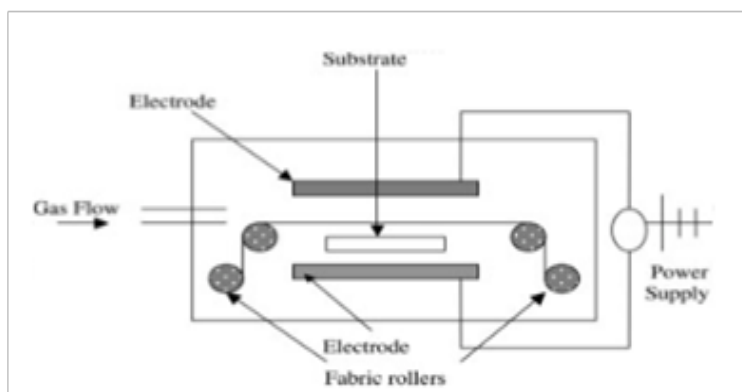


Fig. 2. Inner chamber of the atmospheric plasma facility. Plasma was generated between two electrodes embedded in the dielectric material to form a dielectric barrier discharge.

TABLE 1. Plasma gases and their applications [3].

| Plasma gas | Application |
|---|--|
| Oxidizing gases (O_2 , air, H_2O , N_2O) | Removal of organics by oxidation and to leave oxygen species in the polymer surface |
| Reducing gases (H_2 , mixtures of H_2) | Replacement of F or O in surfaces, removal of oxidation-sensitive materials, conversion of contaminants to low MW species that do not polymerize or redeposit on adjacent surfaces |
| Noble gases (Ar, He) | To generate free radicals in surfaces to cause cross-linking or to generate active sites for further reaction |
| Active gases (NH_3) | To generate amino groups |
| Fluorinated gases (CF_4 , SF_6 , and other perfluorinated gases) | To make the surface inert and hydrophobic |
| Polymerizing gases (monomer gases for direct polymerization, Ar or He pretreated) | Polymerization of layers onto substrates by direct polymerization or by grafting on Ar- or He-pretreated polymer surface |

Argon plasma irradiation in presence of styrene was used for PP modification in a specially designed device [4]. The grafted samples were characterized and analyzed. Grafting reaction parameters were studied, and adsorption capacities of PP-g-St fibers using some solvents were studied. The optimum input power (90 W), irradiation time (3 min.) and grafting reaction time (3 hr.) were selected and the grafting percentage of pure St reached 5.7%. Excellent regeneration ability of PP modified >90% were showed and which were effective in cleaning hydrocarbon pollutants from the air.

Activation of non-woven PP in atmospheric plasma apparatus using 2% oxygenated helium followed by grafting GMA/ β -cyclodextrin or HTCC were effective to produce novel antibacterial and tick repellent fabric which were characterized and analyzed [5,6].

Nonwoven PP fabrics were activated with oxygenated DBD plasma and then grafted with 2% nano ZnO, TiO₂ and Ag [7,8]. PP fabric has acquired UV blocking using nano ZnO, TiO₂ and a high antibacterial activity by nano Ag against *S. Aureus*, *K. pneumoniae* and *C. Albicans*.

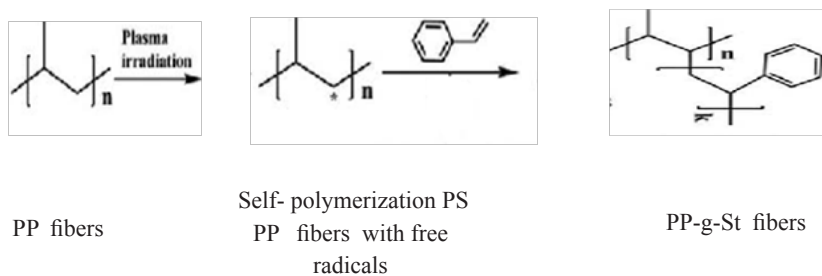


Fig. 3. Reaction of PP-g-St.

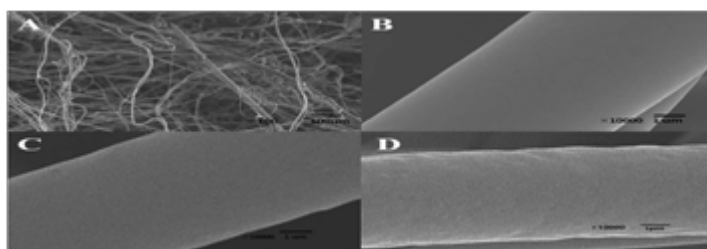


Fig. 4. SEM images of (A) and (B) PP fibers, (C) PP fibers after plasma irradiation, and (D) PP-g-St fibers.

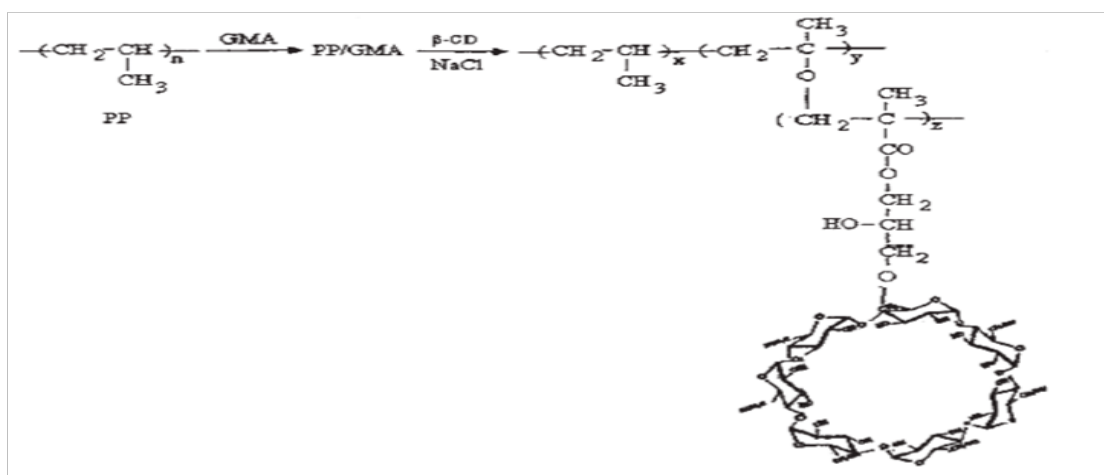


Fig. 5. Grafting CD onto PP/GMA, after PP plasma treatment.

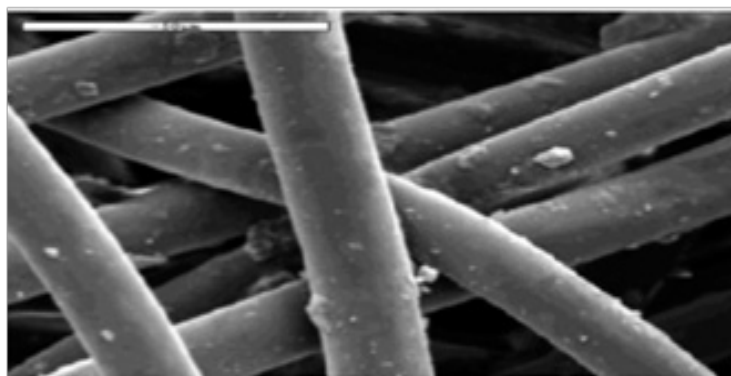


Fig. 6. SEM micrograph for PP/38 % GMA/ 7.2% CD (1000X).

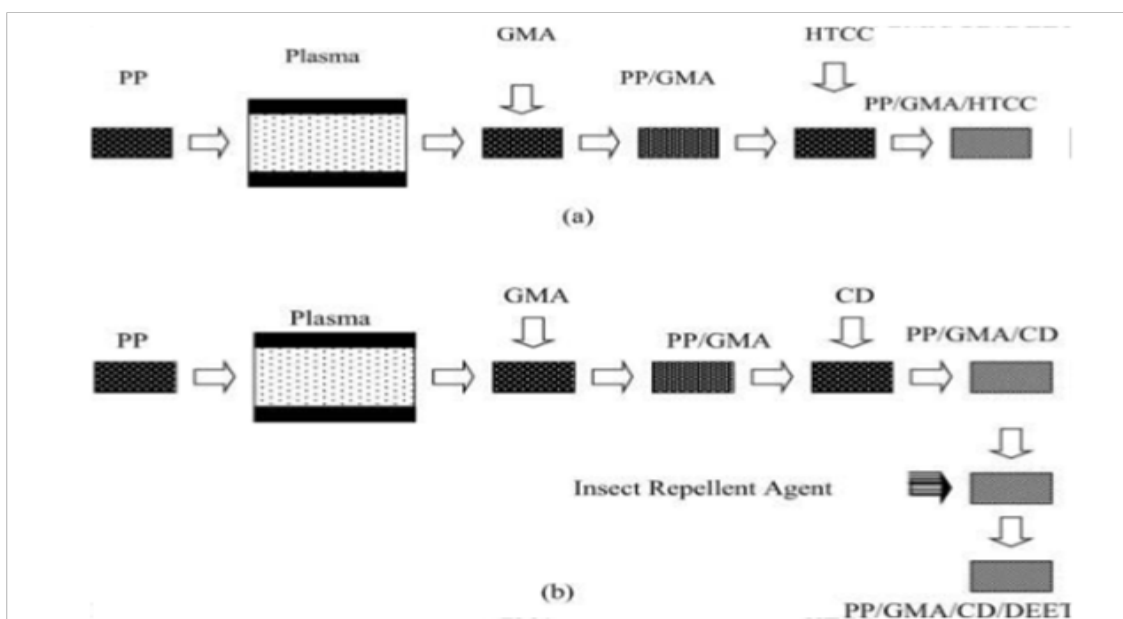


Fig. 7. Plasma-grafted copolymerization process. Path one (a) shows PP/GMA/ HTCC production. Path two (b) shows PP/GMA/CD production followed by inclusion of insect repellent agent.

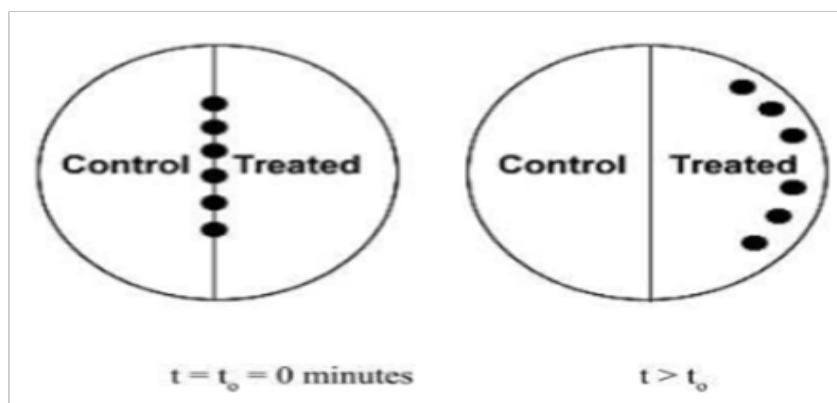


Fig. 8. Arrangement for tick repellence assay. Two equal size (1.4 cm^2) pieces of fabric were placed in the arena centre and six ticks were introduced in the centre where the fabric samples exist. The distribution of the ticks was recorded at 0.5, 1, 2, and 3 hrs.

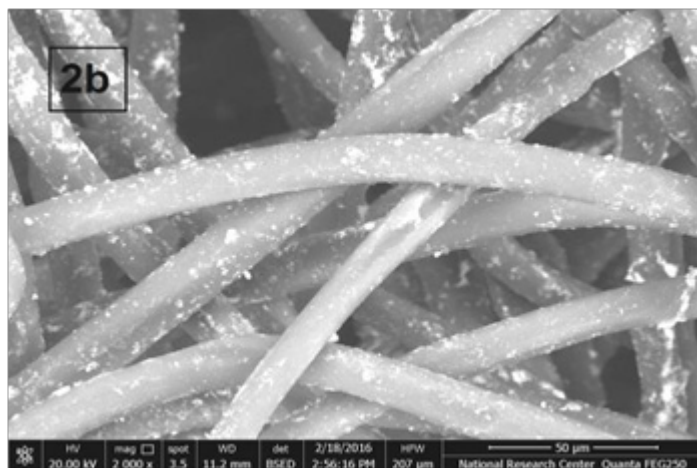


Fig. 9. SEM of PP treated with ZnO (2% owf) after DBD plasma, (2b): mag.2000x.

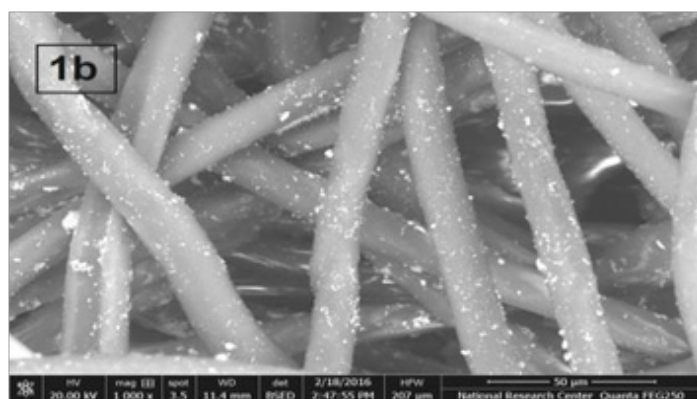


Fig. 10. SEM of PP treated with TiO₂(2% owf) after DBD plasma, (1b): mag.2000x.

TABLE 2. Activation of PP fabrics with DBD plasma followed by treatment with colloidal suspension of ZnO and TiO₂ nano particles and UPF measurement.

| Fabrics | UPF level | Transmittance (%) | |
|-------------------------------------|-----------------------|----------------------|----------------------|
| | | UV-A (315-400 nm) | UV-B (290-315 nm) |
| PP(untreated) | 2.4 (insufficient) | 49.03 | 40.86 |
| PP/ nanoZnO (2%) owf | 38.1 (very good) | 6.93 | 2.38 |
| PP/ nanoTiO ₂ (2%)owf | 17.90 (good) | 8.12 | 5.34 |

TABLE 3. Antimicrobial activity of PP fabrics loaded with silver nano particles.

| Fabric | Percentage reduction of microbial count (as compared to control growth) | | |
|---|--|-----------------------------|-------------------------|
| | <i>Staphylococcus aureus</i> | <i>Klebsiella pneumonia</i> | <i>Candida albicans</i> |
| PP treated with AgNO ₃ (0.058 M) | 92% | 99% | 95% |

Plasma grafting of polypropylene PP[9] using the tetraethoxysilane which has introduced silicon onto the PP surface. The hydrophilicity of the washed TEOS-grafted PP after propylamine exposure was increased compared to the washed TEOS-grafted PP. The plasma treated PP, lost its hydrophilicity after washing almost completely, while the surface hydrophilicity of the TEOS-grafted PP after propylamine treatment has been retained even after its multiple washing and storage 7 days in dry air.

Adsorbents of satisfactory capacity[10] are used for the friendly environment applications. Acrylic acid (AA) was grafted onto bentonite to produce an AA-graft-BT composite using a plasma-induced grafting technique. The modified composite was characterized by different analysis methods. The influencing factors, including contact time, pH value, ionic strength, temperature, and initial concentration were investigated. Compared with previous adsorbents, AA-g-BT has important applications in treating U(VI)-contaminated solutions.

First, ZnO nanoparticles were encapsulated by: poly(AA) or a poly(MMA-co-MA acid) copolymer. Subsequently, PP substrates were activated using plasma treatment. Finally, plasma-treated surfaces were immersed in solutions containing the encapsulated nanoparticles dispersed in an organic solvent and allowed to graft onto it. The presence of nano particles on the substrates was done by different analysis methods[11]. The ZnO-functionalized substrates have exhibited an antibacterial response to *Escherichia coli*.

Nithakalyani *et al.*[12] have assessed the antibacterial activity of herbal surface modified
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PP nonwoven fabric against bacterial wound pathogens. The herbal-coated fabric showed 99% bacterial reduction which is tested according to AATCC 100 method. The antibacterial activity of the herbal extract-modified PP fabric was effective against all the common wound pathogens isolated, with maximum activity against *Staphylococcus* and minimum activity against *Proteus*. The eco-friendly and nontoxic properties of these herbs are promising candidates for medical, health and wound care textile applications.

A new process was an efficient technique for industrial applications and which is known as immersion-pad-pressing-drying-plasma[13]. It was applied to graft a quaternary methyl diallyl ammonium salt on the surface of a polypropylene (PP) nonwoven. Ar and O₂ were the carrier gases for the plasma activation. The optimum acid catalyst concentration was 0.2 M. The grafted PP exhibited excellent antibacterial and hydrophilic properties. The introduction of more peroxides or carboxylic acid groups into PP nonwoven, has shown that the graft ratio for the processes with O₂ as the carrier gas was demonstrated to be higher than with Ar. The modified PP fabric obtained has antibacterial and hydrophilic properties higher compared to PP fabric made by the traditional process. The process overcomes the disadvantages of the conventional plasma process.

Accelerated electron beams

Accelerated electrons are emitted as β -rays by strontium 90 or tritium. Isotopes were used few cases as a source of electrons for the radiation chemistry of polymers. Researches were performed using a powerful beam emitted by electron accelerators high voltage. Electron

accelerators of 300-500 kV are available with increased beam currents which result in even faster production rates at lower costs. High energy electrons of β -rays and γ -rays are quite different, although the end results of interaction with the substrate are the same. Electron beam irradiation, as in case of γ -irradiation, is done by either pre-irradiation or mutual irradiation techniques, but the pre-irradiation is of more importance.

An adsorbent was synthesized by post irradiation grafting of acrylonitrile (AN) onto a non-woven thermally bonded PP sheet using 2 MeV electron beam accelerator[14]. Grafted poly AN chains were chemically modified to convert a nitrile group to an amidoxime group, a chelating group responsible for metal ion uptake from an aqueous solution. Variables such as dose, dose rate, temperature, and solvent composition on the grafting extent were studied. PP modified with the amidoxime group was tested for its suitability as an adsorbent for removal of heavy metal ions such as Co^{2+} , Ni^{2+} , Mn^{2+} , and Cd^{2+} from aqueous solution. Adsorption isotherms were used to study the type of adsorption of these ions. The adsorption capacities of the adsorbent for the metal ions were found to follow the order $\text{Cd}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$.

Styrene grafted onto PP films[15] was done with higher grafting yields when protic-polar solvents are used instead of polar solvents. It is clear that for low dose rates with solvents such as n-octanol and for high dose rates with solvents such as n-butanol was effected. Electron solvation so seems to play an important role in the grafting process. The higher styrene grafting yields are dependent on the physical properties of the solvent exposed to radiation.

Grafting AN onto PP was done using the pre-irradiation electron- beam method [16]. A higher degree of grafting was attended by dilution of AN with DMF than methanol and ethanol which gave a lower degree of grafting. The addition of sulfuric acid to the grafting mixture enhanced the degree of grafting and was an effective method for giving a graft copolymer at low pressure. The grafting reaction depended on the efficiency of the trapped radicals for initiating the grafting reaction and on the monomer diffusion rate toward the grafted layers. The activation energy of the grafting reaction was 21.9 kJ/mol. The absorption peaks of cyano groups appeared in the IR spectrum of PP grafted and the thermal stability of grafted PP increased with increase the graft yield.

Mosleh et al.[17] irradiated PP by electron beam followed by grafting 2N-Morpholino ethyl methacrylate. then, The modified fabric was quaternized with benzyl chloride, monochlorosulfonic acid and chloroethanol. The modified fabrics were sufficient hydrophilic to absorb Cu^{+} from CuSO_4 solution and their antimicrobial properties were performed.

To protect the environment and public health, it is necessary to reduce the pollution caused by cigarette smoke[18]. A novel polymeric filter tip was obtained by modifying PP fiber matrix using two-step electron beam irradiation method. The composite filter tip can absorb more toxic organics in cigarette smoke, which exhibited better absorption capacity, filtration efficiency, mechanical properties and thermal stability than the blank. The enhancement in filtration added absorption performance is effective for minimizing cigarette smoke pollution in air.

Propylene homopolymer (PP1), polypropylene- polyethylene block copolymers (PP2, PP3) and their mixtures with 3 wt.% of bisphenol A dimethacrylate (BPDMA) cross linking agent were irradiated with 25–150 kGy accelerated electrons and were compared[19]. Increased elongation in the presence of was contributed to the cross-linked moieties of PP and the cross-linking agent. The shrinkage stresses were comparable to that of polyethylene based heat-shrinkable material.

Methyl acrylate (MA) was grafted onto PP nonwoven fabric through electron beam irradiation[20]. Gel permeation chromatography analysis showed that the active species survived within the PP fibers for several hours. The survived species can initiate another grafting reaction by changing the conditions. The analysis proved that the grafting proceeds at the surface and interior of Sugo et al.[21] have modified PP by a grafting method. PP were irradiated at 20 Mrad electron beam then grafted with styrene. The grafted when sulfonated with ClSO_3H have an exchange capacity 3.1 milliequivalent/gm which was capable of absorbing ammonia gas and acting as cation exchanger.

Gawish et al.[22] have irradiated PP by an electron beam accelerator and the fabric was grafted with an aqueous solution of 2 N-Morpholino ethyl methacrylate (MEMA). The graft yield was found to be 10-75%. The dyeability with acid dye was highly increased

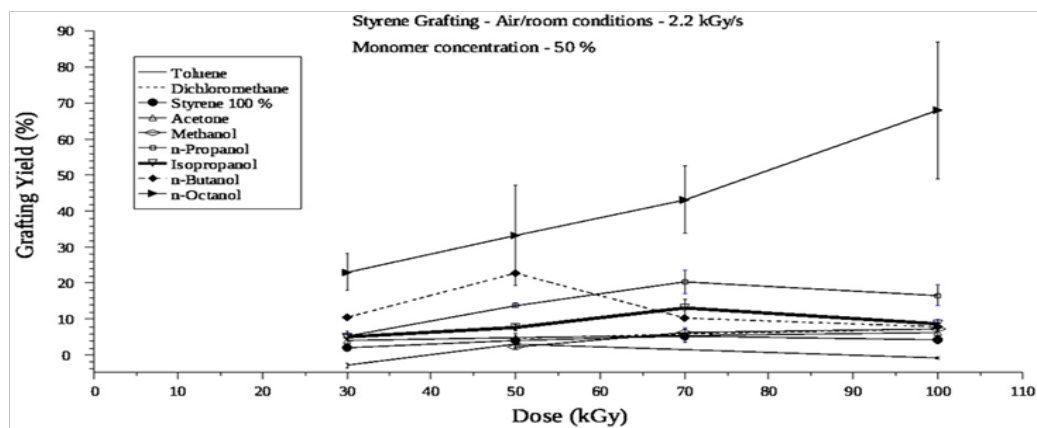


Fig. 11. Styrene grafting yield for polypropylene mutual electron beam irradiation at 2.2kGy/ and 251oC. Grafting medium:1:1 styrene/organic solvent mixture.

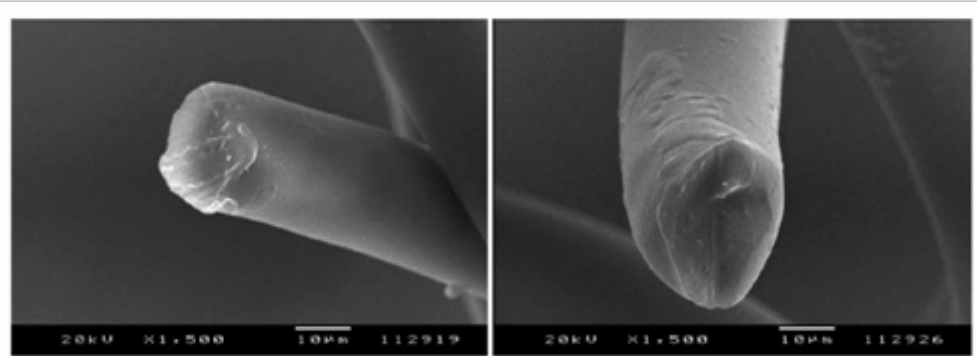


Fig. 12. SEM images of (left) ungrafted (right) AN-g-PP91% graft yield.

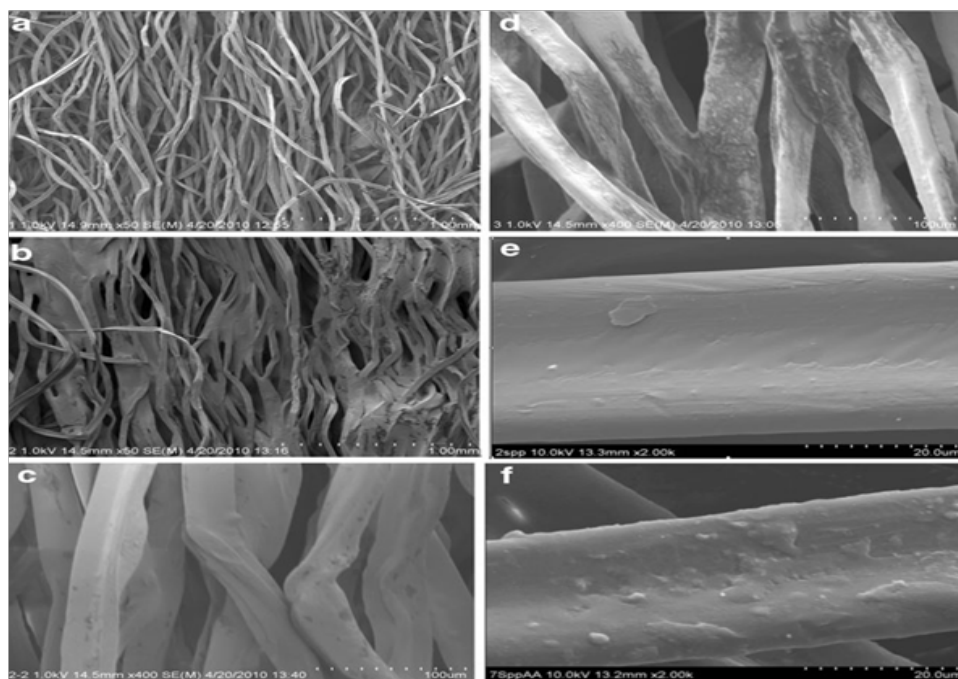


Fig. 13. SEM images of (a), (c) original PP fibers, (b), (d) PP-g-(AA+AMPS) with grafting degree of 16.54 %, (e) original PP fibers after smoking test.

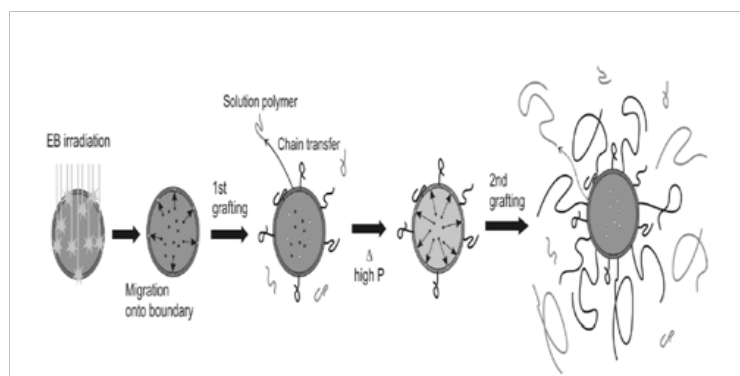


Fig. 14. Two-steps polymerization using "survived" radicals.

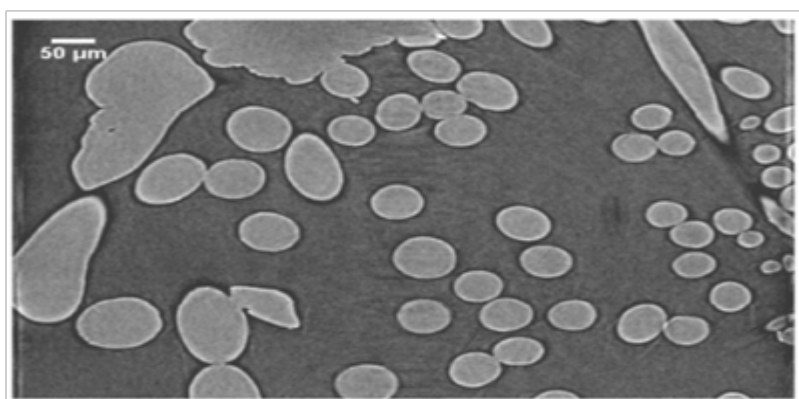


Fig. 15. High-resolution X-ray microscope image for cross-sectional view of MA-grafted PP nonwoven fabric (degree of grafting: 427%).

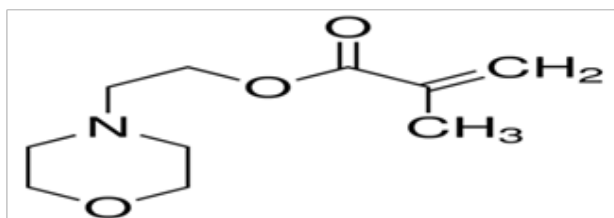


Fig. 16. 2N-(Morpholino) ethyl methacrylate (MEMA).

due to grafting PP with MEMA. PP grafted with MEMA was then quaternized[23] with different alkylating agents such as dimethyl sulphate, allyl bromide, ethyl iodide, 1-iodo hexane. Moisture regain attains 7.6 % compared to 2.24% for PP

non quaternized.

Irradiated PP was affected by an electron beam accelerator[24,25] and the fabric was then grafted with aqueous solutions of either

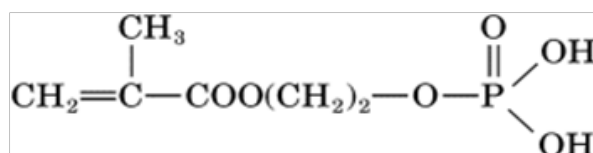


Fig. 17. 2-ethyl methacrylate phosphoric acid (EMPA).

AA or ethyl methacrylate phosphoric acid. Homopolymerization was controlled by addition of CuSO_4 . Results of the polymerization and the graft yield indicated an increase in the moisture regain in comparison to the blank. The modified PP fabric using either monomer behaved as an ion exchange.

Fujiu [26] showed an improved PP uniform grafting by first irradiation webs using electron beam. The pre-irradiated were subsequently dipped in aqueous solution of monomers containing Mohr salt and finally heat-treated either by microwave or by steam at 100°C . The graft-weight increased to 35% for surface and 39% for core which were obtained using the microwave treatment, versus 5% and 26% respectively, for the steam treated.

Einsele [27] studied the grafting of PP with various monomers using different techniques as follows:

a- Pre-irradiation with an electron beam and then graft polymerized in aqueous solution.

b-Simultaneous irradiation by electron beam and graft polymerization in aqueous solution.

Results have shown that greater dye penetration depths were obtained using the pre-irradiation method than using the simultaneous one.

PP/AA-grafted are easily dyed using cationic dyes. Cross-linking of the AA grafted with metal salts was enhanced. In addition, thermal stability of the and the melting point were increased by addition of metal salts. The dyeability of the with disperse dyes was increased by grafting by vinyl amides such as vinyl pyrrolidone and vinyl caprolactam.

Irradiation by ozone

Polypropylene fabric was treated [28] with ozone 13 gm/hr in a flow of oxygen as a carrier at 600L/hr, at room temperature for a fixed time period (one or two hours). The ozone modified fabric was copolymerized with an aqueous emulsion of styrene in a concentration range 0.05-1M and at temperature 100°C . The graft yield was studied and found to be an exponential function of the styrene concentration and depend on the ozone time treatment. The mechanical properties were determined.

UV irradiation for photochemical graft

polymerization

The photochemical graft polymerization is employed for surface modification of PP.

Enhancing oil-sorption performance of polypropylene by surface modification via UV-has induced graft polymerization of butyl acrylate [29].

γ Pre-irradiation technique

Gamma rays are highly used in polymer chemistry. The most widely spread γ rays emission is Co^{60} . It produces γ -rays of approximately 1.2 Mev. quantum energy. Radiation energy is of very high penetrating power. Dose rates are produced by several kilocuries activity range from 10^3 to 10^4 rad/min. It is an efficient initiation method for inducing graft copolymerization by a great number of vinyl monomers. Grafting by this method is done by two main techniques namely pre-irradiation and mutual irradiations technique.

The method involves irradiation of the dry PP fabric alone in air and then it is put in contact with the monomer either as liquid or gas. Grafting is done by the addition of the monomer to the trapped radicals initially formed onto PP fabric and decomposition of the formed hydroperoxides, any monomer can be grafted by this technique.

Chemical modification of polypropylene (PP) fibers by graft copolymerization with vinylimidazole and acrylonitrile was carried out using γ -radiation [30]. Reaction conditions including irradiation dose, comonomer concentration and composition and type of solvent, affecting the degree of grafting were studied. The suitable diluent for obtaining reasonable graft copolymer yield was acetone. The higher grafted yield was achieved by increasing the amount of vinylimidazole in the comonomer feed solution as well as irradiation dose. The derivatives of PP-g-P(VIm/AN) grafted fibers of different functional groups were produced by treating the grafted fibers with various organic agents containing reactive amino groups. Characterization of the graft copolymers and their chemical treatments with different amines was also done. It was observed that the nitrile group in PP-g-P(VIm/AN) polymer undergoes simple addition reaction via nucleophilic interaction mechanism to produce the corresponding PPgraft- P(vinylimidazole/acrylomidine) derivatives. The modified fibers can absorb some metal ions such as Cd, Hg, and Pb from their individual and mixture solutions was calculated.

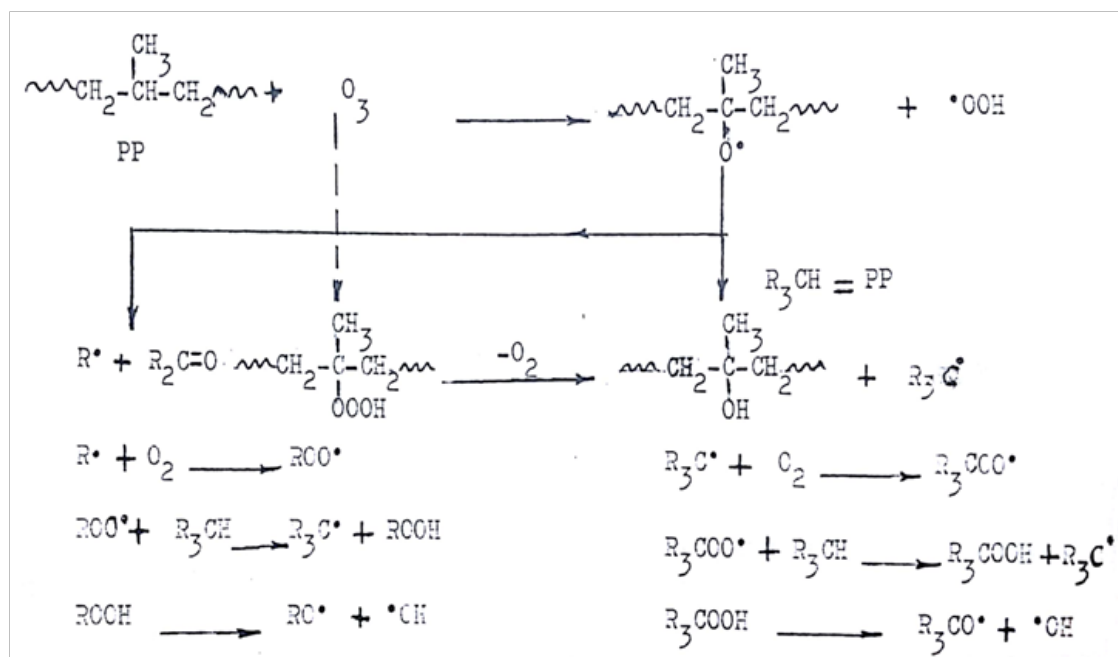


Fig. 18. Reaction of ozone-oxygen mixture with PP.

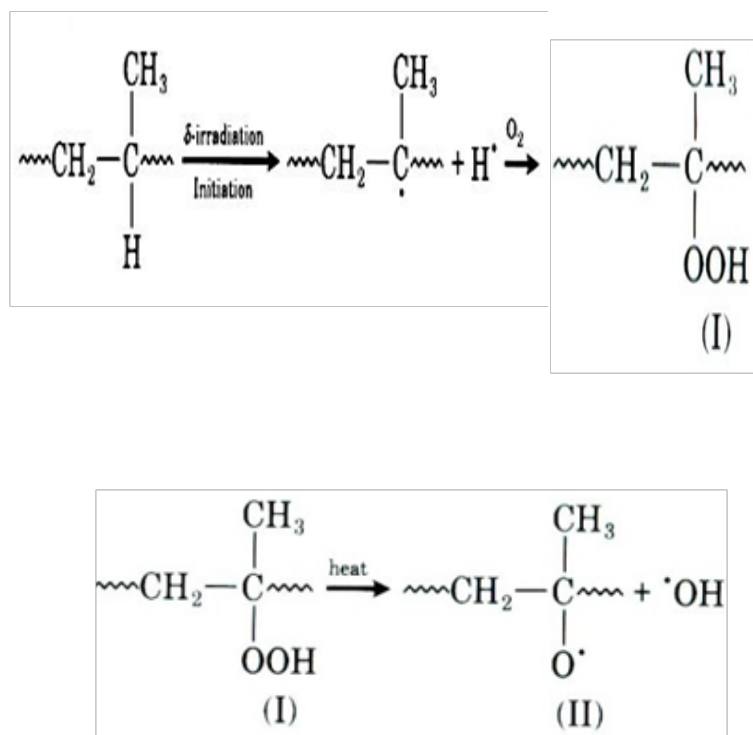


Fig. 19. Gamma irradiation and free radical formation onto PP.

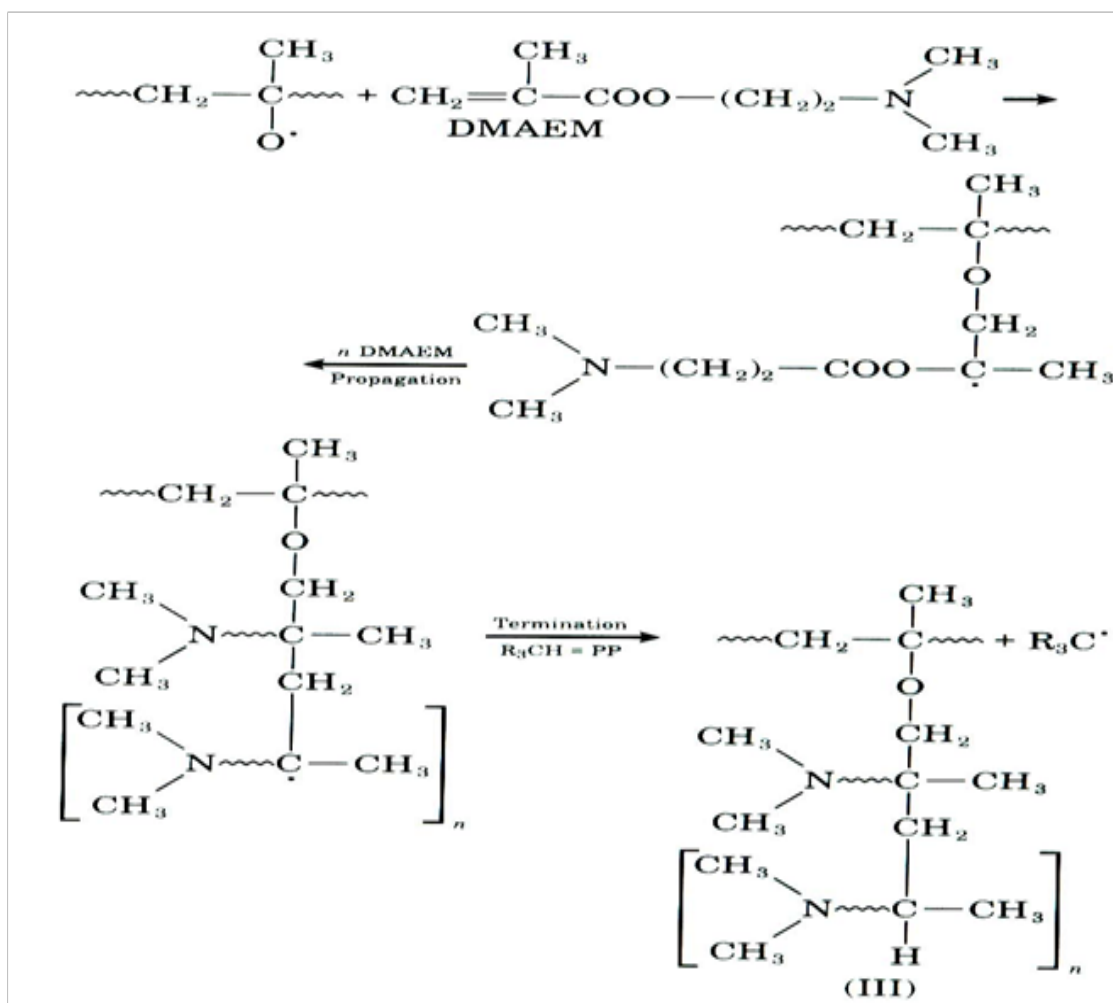


Fig. 20. Grafting of 2-(dimethylamino) ethyl methacrylate into gamma irradiated fabric.

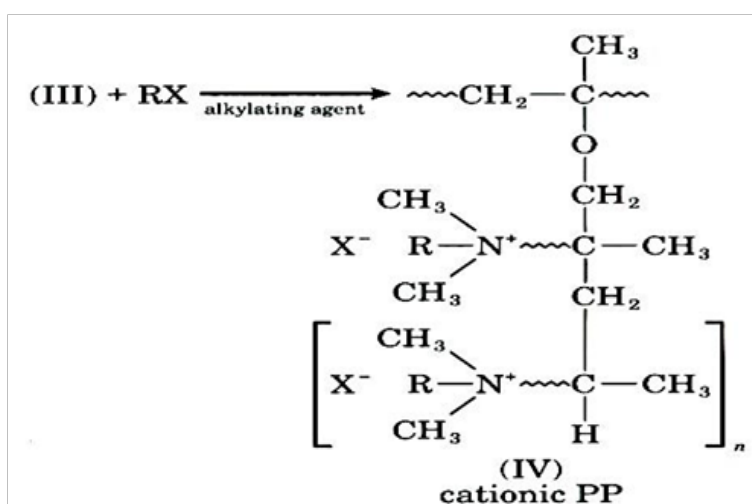


Fig. 21. Quaternization of PP.

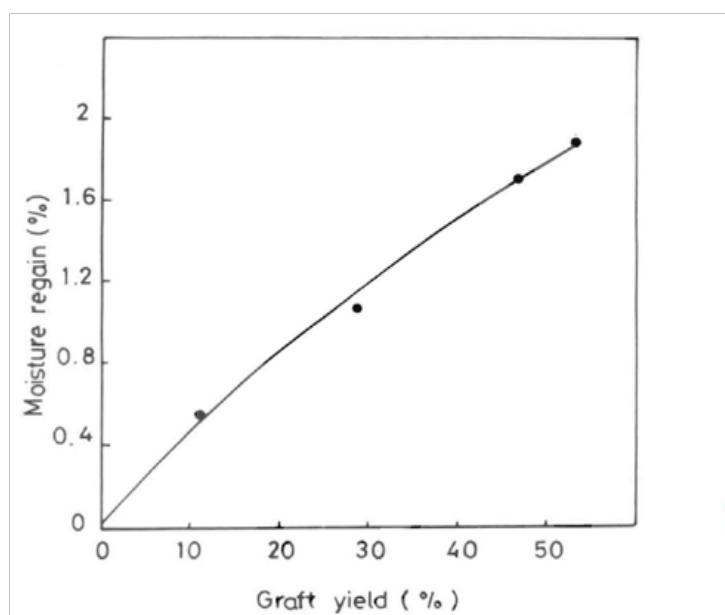


Fig. 22. Effect of MEMA graft yield on PP moisture regain.

Gawish et al.[31,32] grafted aqueous 10-40 % at 50-100 °C of 2-N(dimethyl amino) ethyl methacrylate (DMAEM) and 2N- Morpholino ethyl methacrylate (MEMA 10-20%) at 50 -100 °C into initially gamma irradiated PP. The modified PP was further quaternized with dimethyl sulfate or monochloro acetic acid. The overall reaction is summarized as follows:

Mehta et al.[33] grafted-copolymerized

soluble vinyl monomers into PP which were grafted with acrylic acid (AA) and acrylamide by the pre-irradiation method in water and water/methanol solvent. Water was the best solvent for maximum grafting and acrylic acid was more reactive than acrylamide for graft copolymerization.

Literature review revealed that Misra et al. clarified [34] that isotactic PP was grafted with methyl methacrylate or ethyl methacrylate

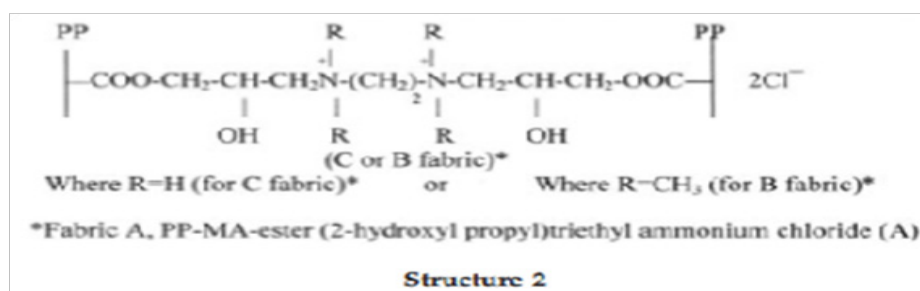
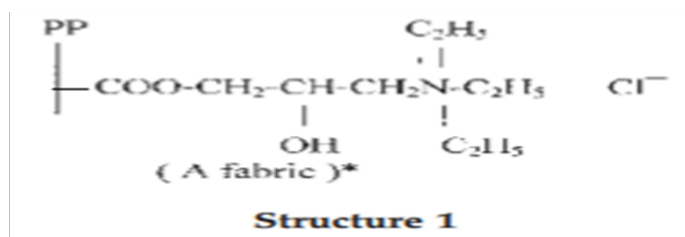


Fig. 23. Amphoteric PP fabrics.

using γ -rays 60 Grafting was found to increase sharply with the irradiation dose increase then decreased. Grafting was function of the monomer concentration and was enhanced by addition of ferrous ammonium sulphate and water was a good medium for grafting. The thermal stability of the grafted polymers was higher than the blank.

Synthesis, characterization and application of novel grafted amphoteric PP fabrics were performed by Mosleh *et al.*[35,36].

PP for biomedical application was produced[37] by irradiation and then grafting 2-hydroxy ethyl methacrylate.

Mutual γ irradiation technique

Grafting a mixture of acrylamide AM, AA and MAA onto PP by mutual irradiation method have been developed by Rao *et al.*[38]. The grafting extent of AM was low, were as in a mixture the amount of AM content of copolymer was higher than the feed ratio. The results are explained on basis of chain transfer mechanism with MAA acid and MAA mixtures. The rate of grafting decreased by increasing the concentration of AA in the feed ratio. It was explained on the basis of the formation either a 3-dimensional network structure or a highly branched structure involving backbone PP molecules with AA which prevents the diffusion of the monomer from the solution phase to the swollen phase.

Mukherjee *et al.*[39] have demonstrated that PP were grafted with (MAA) using simultaneous γ -irradiation method. Grafting was studied and the results are calculated in terms of solvents, swelling behaviour of PP and the extent of homopolymerization. An accelerative effect on the rate of grafting was observed when benzene was partly replaced by methanol. An increase of methanol concentration results in a sharp decrease in the rate of grafting. No grafting occurred in pure methanol. This behaviour was explained in terms of the inhibitory polymerization action of methanol in MAA and the extent of swelling of PP in various benzene-methanol mixtures.

Chemical initiation by a redox method

Chemical initiation is used for grafting of PP with vinyl monomers. This method is not as successful as the radiation method and other different initiation means. It is attributed to the hydrophobic character of PP and low swelling of such in aqueous solution.

Yao Z. *et al.*[40] have used the above method

for graft polymerization of MAA (methacrylic acid) or AA onto PP by a continuous pre-soaking process under nitrogen. AA was grafted on the surface of the at various monomer concentrations of the pre-soaking solution. Acceptable grafting rate was obtained with 0.5-0.8 M AM or 1.5-2 MAA and 0.2 M benzophenone as initiator in the pre-soaking solution.

PP was grafted with vinyl acetate (VA) to give PP/VA copolymer [41]. It was done by heating (1:1) atactic PP for 6 hrs in a VA water emulsion (1:3) and in the presence of 0.5% benzoyl peroxide as initiator. Polyvinyl alc. (0.1%) was used as a dispersing agent for the VA/water mixture. The reaction temperature was 70°C. The yield of the VA/PP copolymer increased after an initial induction period, very rapidly with prolonged polymerization and then level off at 70-80% graft yield. The grafting degree increased linearly with increasing reaction time. The glass transition temperature of produced graft copolymer decreased with decreasing the amount of VA in the copolymer.

The effect of addition of chlorobenzene at a grafting yield was determined[42]. An aqueous suspension of PP was grafted with AA in an aqueous solution containing chlorobenzene as an organic solvent and benzoyl peroxide as catalyst. It gave a graft copolymer with 98% grafting yield. A blank synthesized without the addition of chlorobenzene had 61% graft.

Non-stretched polypropylene yarn [43] treated with a solution containing AA, azo-bis-isobutyronitrile and lauryl trimethyl-ammonium chloride, cationic emulsifier and steam-treated at 110°C to obtain a graft polymer having a graft yield 4.1%. On the other hand graft copolymerization of the stretched PP indicates 2% grafting degree. These results indicated that the used catalyst is not the proper one as compared to benzoyl peroxide.

Modification of PP by other means

Polypropylene (PP) fibers waste was modified by the reaction with concentrated H₂SO₄ [44]. The different analysis methods showed that sulfuric acid at about 105 °C reacts with PP to produce mainly surface sulfonic groups. These SO₃H groups decompose to form SO₂ gas leading to an aromatization of the polymer to form amorphous and graphite carbon. Adsorption isotherms of the cationic molecule, methylene blue showed that the modified PP fibers have a great potential as ion-exchange adsorbent.

Modification of the hydrophilic properties[45] of PE-coated-PP non-woven fabric was done by the use of water-soluble biodegradable polymer produced from carboxymethyl cellulose (CMC) together with AA monomer. Modified fabric hydrophilicity was examined in terms of water uptake. The water uptake (%) of the modified fabric was improved compared to that of the blank. Also, the analysis confirms the complete adhesion between the fabric and the coated layer. Tensile strength increases with increasing coating (%) while elongation decreases. The modified fabric efficiency toward metal ions and dye waste removal was calculated by the removal of Cu(II), Co(II), and Ni(II) ions from aqueous solutions. The results showed that the highest percentage of dye sorption was in the case of basic dye and the lowest one in the case of reactive dye.

PP-knitted fabrics were modified by β -cyclodextrine and cross-linked by citric acid (CTA) [46]. The poly CTA- β -CD polymer-coated fibers were wash resistant. The rate of immobilized CD was controlled by temperature and curing time. The weight increase of the modified fabrics with native β -CD and CTA reached 30 %wt. The treated PP fabrics were dyed using disperse, acid and reactive dyes. Washing fastness was conducted and showed that all dyes were attached, because of inclusion complication with immobilized cavities on the one hand and sorbed hydrogen and ionic bonds that occurred between the poly CTA- β -CD coating and the tested dyestuffs on the other hand.

Modification of PP by nano particles via extrusion and melt spinning machine

Incorporation of Ag, Zn and ZnO, TiO₂, Cu,

CuO₂ nano particles into the melt of the extruded yarns, gave antibacterial and antistatic properties. Nonwoven fabric produced from these yarns are used as wound healing dressings [47-49].

PP was mixed with copper metal nano particles using melt blending in order to produce antimicrobial plastic materials[50]. Antimicrobial is controlled with nano particles concentrations higher than 10 v/v % which decreased 99% of the bacteria in less than 2 hr. Copper oxide nano particles were also added to PP giving stronger antimicrobial behaviour than metal copper nano particles[51,52]. Surface modification of PP nonwoven fibers was done with TiO₂ nano particles [53]. (PP) melt blown fibers were coated with titanium dioxide (TiO₂) nano particles using layer-by-layer deposition technique. The fibers were first modified with 3 layers of poly(4-styrenesulfonic acid) and poly(diallyl-dimethyl ammonium chloride) to improve the anchoring of the TiO₂ nano particle clusters.

Properties of modified polypropylene

Electrical conductivity of PP grafted [54] with MAA, VA and AN was measured for the conditioned at various relative humidity. Electrical conductivity increased in all three modified polymers. The increase in the conductivity of PP grafted with MA acid was two orders magnitude higher than the blank, while the increase in other cases was small. The results were explained on the basis of chemical structure of the grafted. Electrical conductivity increases with respect to MAA graft is due to charge migration and electronic conductivity. For the other two monomers, grafted PP. increase is due to electronic conductivity.

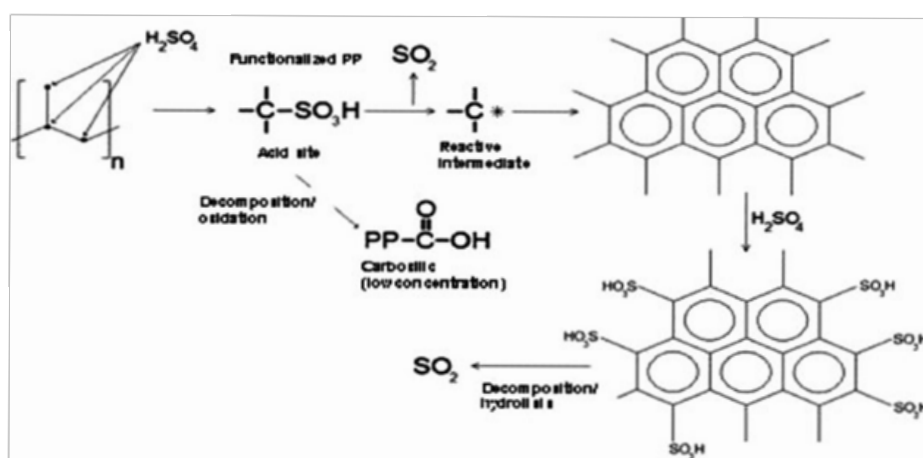


Fig. 24. Reaction of PP with H₂SO₄.

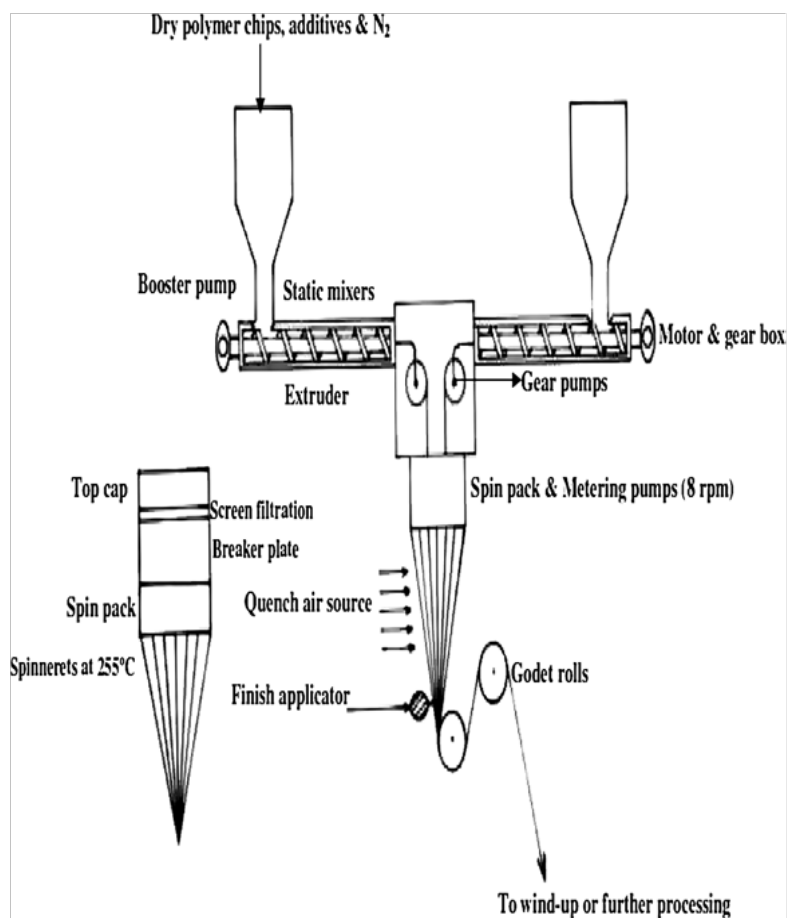


Fig. 25. Bi- components of extrusion melt spinning machine.

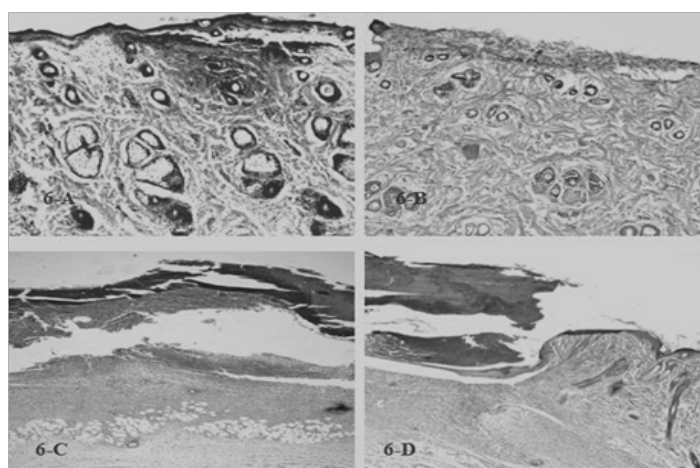


Fig. 26. a) PP/Ag dressed incision wounded rat skin, on day 5, showing re-epithelialized epithelium with underlying dense inflammation. b) Undressed incision wounded rat skin, on day 5, showing epithelial ulceration with loss of all epidermis layers and fibrin deposition at wound site. c) Blank PP dressing applied to incision wounded rat skin, on day 10, showing wide epithelial ulceration, extensive haemorrhage and underlying dense inflammation and granulation tissue formation. d) Ag-SD (silver sulfadiazine) cream dressing applied to incision wounded rat skin, on day 10, showing partial epithelial ulceration, congestion and haemorrhage with underlying granulation tissue formation (H & E X100).

Electrokinetic properties of methacrylic acid (MAA), acrylonitrile (AN) and acrylic acid (AA) graft PP were measured in the presence of cationic dyes [55,56]. The results are explained on the basis of cationic dye adsorption on the grafted in case of MAA graft. But for AA and AN grafted, it is due to the strong attraction of cationic dye to the nitrile group of the grafted.

Conclusion

Modifications of PP products (fibers or fabrics) were done by different irradiation means and then, grafting actively selected vinyl monomers were produced which improved to a great extent PP functional properties. Thus PP hydrophilic property was developed and moisture regain increased greatly by irradiation grafting of active monomers such as AA, MA, MAA, DMAEM MEMA etc., since PP is highly hydrophobic in nature. Antistatic, insect repellent and antibacterial properties were induced onto PP. Also, melting point and dye absorption increased by increasing degree of grafting of the chosen monomers. In addition, the electrical conduction of PP increased by grafting methyl acrylate to PP. Ion exchangers were produced from grafted either with monomers having basic groups which are easily dyed with acid dyes or grafted bearing acid groups which react with basic dyes.

PP has cheap price, high mechanical and highly improved properties. It is now widely used in vehicle lining fabric, geotextiles in road construction protection of rivers and sea boards, in packaging, as suture threads, disposable, non-disposable medical products in hospitals, sport and swimwears etc...

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تحسين خواص ألياف البولي بروبيلين بالطرق الأشعاعية والتطعيم أو بتحويلات أخرى

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يتضمن هذا المرجع فكره عن إنتاج خرز البولي بروبيلين ببلمره غاز البروبيلين (فى وجود ماده مساعده) وهو أحد نواتج البترول، ويتم صهر الخرز فى جهاز الغزل الإنصهارى لإنتاج الألياف ثم تحويل الألياف إلى قماش منسوج أو غير منسوج حسب الغرض منه. وتعتبر الياف البولى بروبيلين رخيصة الثمن، وتتميز ببعض الصفات الممتازة مثل مقاومتها للمواد الكيميائية ومتانتها العاليه. وعلى الجانب الأخر فإن لألياف البولى بروبيلين طبيعه هيدروفوبيه ناتجه عن غياب المجموعات القطبيه فى تركيبها الكيميائى مما يودى لعدم إمتصاصها للرطوبه من الجو وصعوبة صباغتها بالصبغات المعتاده. ولهذا السبب يتم تحويل ألياف البولى بروبيلين بالطرق الأشعاعية المختلفه (البلازما، الحزم الألكترونيه، الأوزون، الأشعه فوق بنفسجيه، أشعه جاما)، بغرض خلق مراكز نشطه على سطح الألياف ثم تطعيمها بإستخدام مونومرات مختاره من أملاح الميثاكريلات مثل داي ميثيل أمينو إيثيل ميثاكريلات -2-ن مورفولينو إيثيل الميثاكريلات، إيثيل ميثاكريلات حامض الفوسفوريك، ميثيل الميثاكريلات، هيدروكسى إيثيل الميثاكريلات فينيل الأسيتات وغيره. كذلك دراسة تأثير عوامل التحويلات المختلفه مثل جرعة تشعيع القماش، زمن ودرجة الحرارة تخزينها والخواص الفيزيائيه لقماش البولى بروبيلين المحور المحتوى على مجاميع أمين ثلاثية أو رباعية لتحسين نسبة رطوبة القماش الممتصه من الجو، ودرجة الإنصهار بالإضافة للطباعه بالعديد من الصبغات وكذلك زيادة خاصية التبادل الأيونى والتوصيل الكهربائى ومنع تكوين الكهرباء الأستاتيكية وطرد الحشرات (مثل الناموس وغيرها) ومقاومة الميكروبات.

وتستعمل أقمشة البولى بروبيلين المحتوية على الفضة والزنك وأكاسيد الزنك والتيتانيوم كارابطه معالجته للجروح .