

A Short Review of Hydrophilic Surface Modification Methods for Low Density Poly Ethylene

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Abstract —In this review, the effect of chemicals, flame, radiation, grafting and their combination on the surface of low density polyethylene (LDPE) were studied. Like most of the polymers, LDPE is inherently hydrophobic; we explored the possible options for rendering the polymer surface hydrophilic without changes in bulk properties of the polymer producing improved wettability mainly due to introduction of function group moieties. It was concluded that wettability was associated with concentration and types of functional groups and consequent changes in the contact angle. It was also found that each method for introducing hydrophilicity has advantages and disadvantages of its own and a combination of methods can be applied catering a specific demand. This introduction of wettability would greatly benefit in enhancing innovative use of LDPE in industrial end products like wetting agents, protective films, anti-static fibers, antifogging surfaces, printable polymers and many others related goods.

INTRODUCTION

Polyethylene is one of the highest consumed plastic, more than 70 million tonnes per year. In the year 2005 total capacity and consumption of polyethylene were 72.7 and 56.7 million tonnes respectively. Various grades of polyethylene include Low density polyethylene (LDPE), Very low density polyethylene (VLDPE), linear low density polyethylene (LLDPE), Medium density polyethylene (MDPE), High density polyethylene (HDPE) and Ultra high molecular weight polyethylene (UHMWPE).

Low density poly ethylene (LDPE) is made from ethylene by using high and low pressure chain growth polymerization process, along with high temperature ranging from 160 to 250°C to accelerate radical generation process usually initiated by Azo bis iso butyronitrile or benzoyl peroxide commonly known as AIBN & BPO respectively. LDPE has a physical density of 0.915 to 0.925 gm/cc, crystalline up to

45%, having melting point from 110 to 115°C and is soluble in toluene and tetra hydro furan above 60°C. The free surface energy of polyethylene is 10 J (at 20 °C). The critical surface tension for LDPE ranges between 25.5 and 36 mN/m [1].

LDPE possesses good mechanical, thermal and chemical properties, well suited to make products with economical demands, however its low surface energy values i.e. lower than 30 Mj/m² represent important problem in making product with desired surface properties [1], more than 70% of polyethylene require surface refinement before they are further processed. Untreated LDPE is hydrophobic due to its non-polar surface; however there are many benefits of introducing polar groups upon the surface to make the polymer hydrophilic as LDPE films are in high demand in technological sectors like electronics, automotive and aerospace. To quote a few benefits of modification of surface structure include interfacial fracture toughness, higher adsorption, better adhesion, biocompatibility and less surface tension. These changes in surface will impart advantages in industrial applications including paints, coatings, adhesives, lubricants, polymer blends, protective agents, antistatic films, printable surfaces and membranes. The objective of this paper is to identify and compare various options of LDPE surface treatment such as chemical etching, flame oxidation, corona discharge, plasma treatment, ultra violet radiation and grafting.

EFFECT OF ACIDS

Polyethylene has a high degree of chemical resistance, it is resistant to polar solvents, concentrated aqueous solutions of inorganic salts and mineral acids, and this resistance is directly in relation with percentage crystallinity of the polyethylene. However polyethylene is easily attacked by oxidizing agents mostly acids and increase in temperature also gives support to actions of acids[1]. Action of chemical etching over polyethylene using nitric, sulfuric and chromic acids renders polymers' surface

rough and introduces polar groups onto the surface. The intensity of the induction of new polar groups onto the surface of polyethylene is in direct proportionality to time of etching.

Nitric acid has considerably low effect on the surface of polyethylene in comparison to sulfuric and chromic acids [2]. The fuming nitric acid exposure induce a weight-loss of material (10-70%) depending on crystallinity, it also leaves the crystalline region as a residue producing a high content of micro voids. The polyethylene treatment is performed at 60°C within closed tubes for period of 5-180 hours inducing oxidized groups-COOH, -ONO₂, -NO₂ at the surface. Prolonged expose may lead to significant decrease of polyethylene hardness properties [3].

The effect of fuming or concentrated sulfuric acid is also accompanied by oxidation process; however the phenomenon is complex because of the introduction of several new polar groups. These sulfonic groups are OSO, SO, SO₃H, SOC etc. Sulfonated film samples was prepared by immersing a polyethylene film having size of (3x3 cm²) in 15% fuming sulfuric acid for 5 min at 25°C. The resultant product film were then washed in a series of baths first 5% sulfuric acid; concentrated H₂SO₄, 50% H₂SO₄; water; and finally acetone and then dried in a vacuum at 25°C producing a contact angle of 63° and SO₃H concentration of 5x10¹⁴ groups per centimeter square[4].

Similarly, the chromium in chromic acid initiates by forming chromium ester intermediate finally hydrolyzing to alcohol. Other groups containing carbonyls, such as aldehydes, ketones and carboxylic acid are also produced by the action of chromic acid [2]. James R Rasmussen et al in their pioneering work functionalized the surface of LDPE by initial oxidation with chromic acid and then subsequent reaction with 70% aqueous nitric acid at 50°C to dissolve inorganic residues, produced polyethylene whose surface contains moieties of carboxylic acid approximately 60% and ketones or aldehydes approximately 40% as only significant functional groups. The majority of the surface carbonyl groups produced by this method were firmly attached as chromic acid oxidation of polyethylene to polyethylene carboxylic acid proceeds with cleavage of carbon-carbon bonds. In all of the chromic acid solutions, one with the ratio CrO₃/H₂O/H₂SO₄ in the ratio of 29/42/29 by weight produced functionalized polyethylene with fewest amount of non-carbonyl groups [4]. His functionalization of polyethylene had five considerations, (i) by using polar partially active reagents functionalization will be restricted to surface only, (ii) carboxylic acids can be converted into other useful derivatives, (iii) carbonyl derivatives have strong IR absorption at the frequencies at which polyethylene is transparent, thus well suited for analysis, (iv) application procedures can be applied to variety of forms of polyethylene and (v) to explore several oxidative methods for introducing carboxylic groups onto the surface of polyethylene.

Two distinct methods for identification of location and mobility of functional groups at the surface of oxidized LDPE were produced. The first converts the carboxylic acids of PE-CO₂H to carbonyl chloride using thionyl chloride then generates amides and esters by reaction with appropriate nucleophiles. The second reaction sequence is based on generation of surface carbonyl hydroxide groups from PE-CO₂H with diazomethane and hydrazine hydrate and reaction of PE-CONHNH₂ with electrophiles. These functional groups renders the polymer surface hydrophilic and it remains hydrophilic for extended periods at room temperature, however when heated in air at 90°C -100°C, it rapidly turns hydrophobic but when heated in water, it remains hydrophilic[5][6].

In a recent study in order to improve the interfacial adhesion between copper and low density polyethylene the surface was treated with chromic acid solution with conjunction with oxygen plasma. Treatment time of chromic acid was varied from one minute to one hour at 70°C and oxygen plasma treatment ranged from 30-90 sec. Only when treatment times of both chromic acid and oxygen plasma were greater than 10 minutes and 30 seconds respectively, the contact angle decreased up to twenty degrees [7].

Table 1: Reported densities of surface functionalities [8]

Author	Substrate/ Treatment	Groups/ area	Conc	Method
Rasmussen et al	PE/Chromic acid	2x10 ¹⁵ COOH per cm ²	3.3 COOH nmol/cm ²	Fluorometric
Farley et al	PE/Chromic acid	16x10 ¹⁴ COOH per cm ²	2.7 COOH nmol/cm ²	Titration
Kuhn et al	PE, PP/ O ₂ plasma wet chemical reduction	10-14 OH/ 100 C	0.4-0.5 OH	Derivatization with trifluoro acetic anhydride. (TFAA)
Friedrich et al	Polymers/ Pulsed plasma	1-30 OH/ 100 C	<0.1 -1.2 OH	Derivatization with TFAA
Friedrich et al	Polymers/ copolymerization	1-24 NH ₂ / 100 C	<0.1 -0.9 NH ₂	Derivatization with penta fluoro benzaldehyde

EFFECT OF SURFACTANTS

Surface active agents shortly abbreviated as surfactants are classified as anionic, cationic and non-ionic. Typical surfactant may consist of a linear hydrophobic tail (alkyl) and hydrophilic head group. For non-ionic surfactant the head group may be polyethylene oxide or polyol and for ionic surfactant head group may consist of sulphonic acid salt or quaternary ammonium salt. However a class of surfactants having branched tail (di dodecyl dimethyl ammonium bromide) penetrates the grooves in the polymer surface and wet the surface more effectively. The wetting behaviors of hydrophobic surfaces are

turned into hydrophilic due to the decrease of surface tension by surfactants adsorption onto the interface. For linear tailed surfactant upon attaining hydrophilicity via reduced contact angle stagnates and does not lower with increase concentration of the surfactant, however in case of branched tailed surfactants the decline of contact angle goes on continuously as polymer enters into super hydrophilic range. These two different behaviors are because of the linear tail structure. The contact angle is reduced due to surface tension at liquid-gas interface as both the liquid-gas and liquid-solid interfaces are saturated with surfactant. This happens when surfactant concentration attains or exceeds the critical micelle concentration level, however for branched tailed surfactants surface tension at liquid-solid interface continues decreasing even when surfactant concentration exceeds critical micelle concentration and contact angle onto the rough surface as compared to liquid-gas interface. Periodically, the contact angle lowers at liquid solid interface up to the level that surface is switched into hydrophilic & super hydrophilic range [9]. For the LDPE samples subjected to minute quantity of non-ionic surfactant can considerably effect bio-degradability.

Polysorbate a nonionic surfactant and emulsifier derived from polyethoxylated sorbitan and oleic acid, when applied with a concentration of 0.5% showed increased biodegradation by action of bacteria named *Pseudomonas Aeruginosa* in contrast to untreated LDPE. Whatsoever the effect of surfactants, the main disadvantage still remains that simple rinsing with water washes away hydrophilic properties of the polymer [9] [10].

EFFECT OF FLAME OXIDATION

Flame oxidation on LDPE can be achieved by treating polyethylene surface by a controlled flame produced by mixture of natural gas and air for precise treatment time. This process produces good surface oxidation and high degree of wettability in short time. After rinsing the flame treated sample with water and ethanol, bead-like molecular structures can be observed indicating improved wettability and presence of alcohol, ether and carbonyl moieties. Jing Song et al in their experiment constituted efficient film flame treatment, controlling distance of tip of the flame (0-1mm) with the substrate and treatment time and number of treatments to be done per sample. Reported combustion mixture flow rate was $12.3\text{cm}^3/\text{sec}$, stoichiometric fuel and air ratio was 0.93 moles to 1 mole. Repeated cycles for flame treatment were done to increase the effect of oxidation, the speed of sample was 0.5 m/sec with flame cone length of 1cm and exposure time per cycle was approximately 0.02 seconds. Surface wettability of the treated sample was significantly improved, as reported contact angle decreased to 47.5° from 100° for the sample treated 200 times. Interestingly, no

considerable decrease in contact angle was observed upon washing of the treated samples [11]. In another experiment, adhesion properties of flame treated LDPE were tested on custom built adhesion testing device. After flame treatment, increase polarity of the LDPE surface was recorded with decrease of contact angle from 47° to 17° for a sample treated 200 times. Moreover, increase in adhesion properties was also reported and it was concluded that bonding created by functional group were responsible for better adhesion hysteresis [12].

EFFECT OF CORONA DISCHARGE PLASMA

The low density polyethylene film treated with corona discharge plasma exhibits a prominent increase in surface activation and as consequence wettability properties. M. Pascual et al experimented LDPE exposure to continuous corona discharge with LDPE film moving at velocity of 15 meters per minute generated by FABRILEC model GF-100-BADIA. This equipment operates at 50Hz with maximum power of 1kW. The distance between electrodes was 1.5mm. The plasma treatment was carried out at power of 0.6kW. After treatment, contact angle reduced from initial value of 93.5° to final value of 51.4° . However after ageing of 21 days the contact angle showed increase of 26% and new contact angle was 64.8° , concluding that hydrophilicity achieved by plasma treatment is not permanent. This reversal is due to following reasons; (i) induced chemical groups inter reaction, (ii) diffusion of low molecular weight oxidized material from top layer to interior bulk, (iii) new oxidation with air exposure and (iv) migration of low molecular weight additives of LDPE from bulk to surface [13].

EFFECT OF HOLLOW CATHODE GLOW DISCHARGE

In hollow cathode glow discharge, excitation, dissociation and ionization are efficient due to continuous process, homogenous surface modification, and low gas flow rate. Discharge is confined inside the hollow cathode made of copper or aluminum. Polyethylene substrates were modified by M. Quitzau et al utilizing argon, nitrogen, and their mixture. Treat with argon introduces oxygen to carbon producing C-O and C=O groups. However using nitrogen is used alone or along with argon polar groups C-N and C=N are also induced. Gas phase in plasma gives atoms, free radicals, ions, electrons and photons providing a highly reactive medium. Polyethylene is functionalized, cross-linked and etched after continuous treatment with cathode discharge [14].

EFFECT OF PHOTO SULFONATION

Alkane sulfonation can be achieved by two photochemical processes, sulfoxidation and sulfochlorination. In the methods, sulfur di oxide and an oxidant is used. In sulfochlorination, chlorine acts as an oxidizing agent. Introduction of sulfonyloxy groups on the surface of low density polyethylene or any other polymer by UV radiation produced by mercury lamp in presence of sulfur di oxide and air is termed as photo-sulfonation. The contact angle can be decreased from approximate values of 100° to 30° after the process. However, after ageing process of 30 hours, contact angle increases again to 65°. Samples will revert to their initial hydrophobic position if exposed in air for a long period. Crosslinking process can reduce the mobility of the chain segments and partially stabilizes the surface against hydrophobic recovery [15].

EFFECT OF MONOMER GRAFTING

One of the methods for grafting polyacrylamide onto the surface of low density polyethylene in aqueous dispersion is by the help of free radical initiator. Grafting by solution polymerization is carried in using wetting agent and an additive consisting of alkane with attached thiol functional groups improving wettability of substrate considerably. The temperature at which grafting is performed ranges from 60°C to 110°C and as wetting agent any kind of surfactants may be used [16].

Batich et al in their patent identified that solution polymerization process results in higher weight gain and mostly physical adsorption of the solution onto the LDPE surface. In their method LDPE in fiber, film, granule or powder form was cleaned first and then oxidized by chromic acid solution for 5 minutes at 72°C. After rinsing with HNO₃ solution to remove any organic impurities the samples were washed with deionized water and acetone and dried under vacuum for 4 hours. After drying the samples were exposed to diborane solution in tetrahydrofuran for 18 hours, producing hydroxyl functional groups over the surface of LDPE.

These LDPE samples were grafted with acrylamide using ceric ammonium nitrate as free radical initiator. The process resulted in grafting of acrylamide which covalently bonds to the surface of the substrate considerably increasing the wettability of LDPE [17].

CONCLUSION

Various hydrophilic modification processes of low density polyethylene (LDPE) in film, powder, fiber and granular forms were studied. LDPE underwent these processes showed significant progress in wettability. This was further quantified with reduction in contact angle, which is influenced by concentration

and distribution of polar moieties. It was deduced that with the passage of time, contact angle values showed a partial increase making polymer less hydrophilic. Further need of functional group concentration and permanency is felt for making the hydrophilicity more durable. It is recommended that by introducing more lasting hydrophilic properties in low density polyethylene, new areas such as technical textiles, food packaging, antistatic, anti-fogging and printing properties can be enhanced.

REFERENCES

- [1] Cornelia Vasile, Mihaela Pascu. "Practical Guide to Polyethylene". Rapra Technology Limited, 2005.
- [2] Hao Wang, Shuang Jun Chen, Jun Zhang. Surface treatment of LLDPE and LDPE blends by nitric acid, sulfuric acid, and chromic acid etching. "Colloid Polym Sci" (2009) 287: 541-548.
- [3] M. E. Cagiao, D. R. Rueda, and E. J. BaltA Calleja Hardness of nitric acid treated polyethylene followed by recrystallization." *Colloid & Polymer Sci*". 265:37-41 (1987).
- [4] David E. Bergbreiter and Konrad Kabza. Annealing and Reorganization of Sulfonated Polyethylene Films To Produce Surface-Modified Films of Varying Hydrophilicity. . "Journal of the American Chemical Society". 113, 1447-1448 (1991).
- [5] James R Rasmussen, Erwin R Stedronsky and George M Whitesides. Introduction, Modification, and Characterization of Functional Groups on the Surface of Low-Density Film. "Journal of the American Chemical Society".(1977), 99:14 4736-45.
- [6] James R Rasmussen, David E Bergbreiter and George M Whitesides. Location and Mobility of Functional Groups at the Surface of Oxidized Low-Density Polyethylene Film. "Journal of the American Chemical Society".(1977), 99:14 4746-56.
- [7] Ju-Shik Kong, Dong-Jin Lee and Han-Do Kim. Surface modification of LDPE film and improvement of adhesion between evaporated copper metal film and LDPE. "Journal of Applied Polymer Science", Vol 82 (2001) pages 1677-1690.
- [8] R Mix, K Hoffmann, U Reschgenger, R Decker and J F Friedrich. Covalent coupling of fluorophores to polymer surface-bonded functional groups. "Polymer Surface Modification: Relevance to Adhesion", Vol 4, pp 171-191, Ed K.L. Mittal, 2007.
- [9] Feng Ming Chang, Yu Jane Sheng, Hui Chen, Heng-Kwong Tsao. From super hydrophobic to super hydrophilic surfaces tuned by surfactant solutions. "Applied Physics Letter", 91, 094108 (2007).
- [10] A Chr Albertsson ,Chr Sares, S Karlsson. Increased biodegradation of LDPE with nonionic surfactant. "Acta Polymerica" Vol 44, 5, pg 243-246, (1993).
- [11] Jing Song, Ullrich Gunst, H F Arlinghaus, G J Vancso. Flame treatment of LDPE: Surface chemistry across the length scales, "Applied Surface Science". 253 (2007) 9489-9499.
- [12] Jing Song and G. Julius Vancso. Effects of Flame Treatment on the Interfacial Energy of Polyethylene, assessed by Contact Mechanics. "Langmuir", 24, 4845-4852,(2008).
- [13] M Pascual, R Balart, L Shanchez, O Fenollar, O Calvo. Study of the aging process of corona discharge