Development of Bio/Blood Compatible Polypropylene by Radio-Frequency Plasma Treatment

N. Gomathi[*1,2], S. Neogi[2]
[1]Department of Chemistry, Indian Institute of Space Science and Technology, Thiruvananthapuram, 695547, India
[2]Department of Chemical Engineering, Indian Institute of Technology, Kharagpur 721302, India
* Corresponding author: Tel +91-0471 2568474 Fax : +91-0471 2568406
email: gomathi@iist.ac.in, sivakumar.gomathi@gmail.com

Abstract
In this work, polypropylene surface was modified using various plasmas including argon, argon-oxygen, nitrogen and helium, according to the central composite design of response surface methodology to optimize the process conditions. Increased surface energy and surface roughness helped in improving hydrophilicity of polypropylene. Various functional groups including hydroxyl groups, carbonyl, amine, imine, nitrites, C-O-C incorporated to the polymer surface resulted in improved cell adhesion on polypropylene treated with various plasmas at optimum conditions. Biological results prove that surface modification of polypropylene by plasma treatment constitutes a good route towards the improvement of cell adhesion. Higher cell adhesion and higher viability was confirmed by MTT assay with L929 mouse fibroblast cells. Prolonged partial thromboplastin time after plasma treatment under optimum conditions indicated improved blood compatibility of treated polymeric surfaces. Better adhesive property was observed with helium plasma treated polypropylene which was indicated by higher peel strength. Argon and nitrogen plasma resulted better biocompatibility while helium and nitrogen resulted better blood compatibility among various plasma treatment.
Key words: Polypropylene, RF plasma, Biocompatibility, Blood compatibility

Introduction

Many diverse applications of polymers as biomaterials depend upon physical, chemical and biological interactions at the surface. Polymers find specific applications in various implants including orthopedic implant, cardiac implant, dental implant, soft tissue implant, biosensor and biomedical devices [1]. Nevertheless, they exhibit poor surface properties which necessitate the surface treatment of polymers not only to clean the surface but also to bring the physical, chemical and biological changes. Plasma surface modification is the widely used eco-friendly technique which modifies the surface without affecting their bulk properties. In the present study, polypropylene surface was modified using various plasmas including argon, argon-oxygen, nitrogen and helium. The experiments were conducted according to the central composite design of response surface methodology to study the effect of process variables and to optimize the process conditions.

Materials and methods

Food grade polypropylene sheets were treated with plasma using various gases namely, argon, oxygen, nitrogen and helium. The plasma treatment of the cleaned polymers was performed using a plasma reactor (M-PECVD-1A [S]) procured from M/s. Milman Thin Film Systems, Pune, India. The experiments were conducted at various levels of process variables namely RF power, pressure, flow rate and treatment time to optimize the process conditions. The treated samples were characterized through various surface characterization techniques.

Characterization Techniques

Deionized water, formamide and diiodomethane were used for the evaluation of contact angle performed through sessile drop method using Rame-Hart 500-F1 advanced goniometer (Rame-Hart Instrument Co., Netcong, NJ, USA). The surface energy (γ_s) was calculated by Owens and Wendt method (Owens and Wendt, 1969). FTIR spectral investigation of the polymer samples and surface morphology were performed using a Thermo Nicolet Nexus 870 FTIR (Thermo Nicolet Corporation, North America, Madison, WI) and Jeol JSM-5800 scanning electron microscope (JEOL, Tokyo, Japan) respectively.

Biostudies

Biocompatibility of the samples were studied qualitatively through the examination of the morphologies of adhered L929 mouse fibroblast cells and quantitatively using MTT assay after 72 h of incubation. Blood compatibility of the samples were qualitatively studied through examination of platelet adhesion and their spreading through scanning electron microscopy and quantitatively by measuring the partial thromboplastin time using platelet rich plasma and platelet poor plasma respectively.

Results and discussion

Effect of process variables on surface energy and weight loss

Process variables exhibited their influence on surface energy and weight loss in all plasma treatments except argon-oxygen plasma treated polypropylene. Since none of the variables were found to be influencing the surface energy of argon-oxygen plasma treated polypropylene, it was optimized considering only the weight loss of polypropylene. Plasma surface modification of polymers is a very complex phenomenon and is very difficult to generalize the trend of the effect of process variables on surface energy and weight loss. However the positive and negative effects of the process variables can be justified. Increasing surface energy with increasing power was due to large number of active species in argon plasma treatment while decrease in surface energy is due to the predominant effect of weight loss than functionalization. Positive and negative effects of pressure were observed collectively due to the higher ion density and decreased mean free path respectively. Positive effect of flowrate was due to increased active species at higher flowrate with sufficient ionization while the negative effect was due to poor ionization at higher flowrate due to gas impedance. Optimum conditions determined for various plasma gases are given in Table 1.

Surface chemistry and plasma characterization

Effect of hydrogen abstraction was observed in all cases which resulted in double bond formation. In case of argon and helium plasma no new chemical functionalities were added from the gas phase during plasma treatment but were added during post plasma treatment reaction. Carbonyl and hydroxyl groups were found to be attached to the surface after plasma treatment with argon and helium gases when they were exposed to atmosphere. When they were treated with argon-oxygen plasma, hydroxyl groups were observed but not carbonyl groups due to scavenging effect of reactive oxygen species. Nitrogen plasma treatment of polypropylene was found to attach amine, imine and nitrite groups to polypropylene surface. Various active species responsible for the surface chemistry changes of polypropylene during plasma treatment were investigated through the emission spectrum of the plasma gases. Active species in the form of excited and metastable-atoms and molecules, ions of various gases were observed from emission spectra. Reaction products during plasma treatment such as CO^+, NH, NH_3, CH^+ etc. were noticed from various plasma treatments.

Surface morphology

Increased surface roughness was observed from SEM photomicrograph of plasma treated polypropylene. Argon plasma resulted in more homogeneous etching while nitrogen and helium plasma resulted in deeper and more intense etching. Increased roughness with increasing power and treatment time were observed in various plasma treated conditions.

Table 1: Optimum conditions for various plasma treated polypropylene

Plasma	Power (W)	Pressure (Pa)	Flow rate / O_2 content (sccm/%)	Time (min)	Surface energy (mN m^{-1})	Weight loss (%)	Desirability
Argon	155	16.7	16.9	8	38.7	0.04	0.741
Argon-oxygen	71.26	168.88	16	4	34.67	0.04	0.838
Nitrogen	92.2	175	15.8	4.99	35.6	0.08	0.713
Helium	155	125	10	7.99	37.2	0.099	0.785

Aggregation of granular structures formed around the nano and micro depressions due to bombardment of active species were observed with argon-oxygen plasma
treated polypropylene. Increased deposition of degradation products on polypropylene surface due to better ionization at low pressure and higher flow rate were observed with nitrogen plasma treatment. Helium plasma treatment exhibited localized etching due to preferential etching in amorphous region at lower levels of pressure, flowrate and treatment time.

Adhesive property

Plasma treatment removes boundary layer by increasing their cohesive strength by cross-linking. Besides, removal of weak boundary layers during plasma treatment and chemical interaction between polymer surface and adhesive enhances the adhesive property of polypropylene. Peel strength of untreated and various plasma treated polypropylene is shown in Fig. 1. Increased peel strength of argon plasma treated polypropylene was found to be 43.48% when compared with untreated polypropylene. Compared to peel strength of untreated polypropylene, argon-oxygen plasma treatment exhibited 30.43% increase of peel strength. It may be due to increased surface energy along with increased polarity due to incorporation of OH groups onto the surface. Nitrogen plasma increased the peel strength of polypropylene to 0.37 N mm^{-1} and 60.87%. This may be due to both incorporation of polar groups and increased surface roughness. Compared to argon and argon-oxygen plasma treated polypropylene nitrogen plasma resulted in more enhanced surface roughness. The improved adhesion in the case of nitrogen plasma may be mainly due to the changes in its surface morphology and nitrogen containing groups. Helium metastable with higher excitation potential of 19.8 eV than that of argon plasma (11.5 eV) is in the range of polymer ionization potential (Egitto and Matienzo, 1990). Among various plasma-treated polypropylene helium plasma resulted in more pronounced etching. Moreover increased cross linking by inert gas plasma treatment helps in the removal of weak boundary layers. Thus helium resulted in 60.87% increase in peel strength.

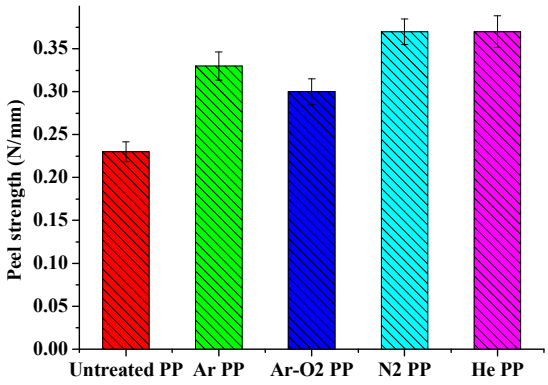

Figure 1. Peel Strength of Untreated and Various Plasma Treated Polypropylene

Bulk property

Thermal studies were performed to study the bulk property changes caused by plasma treatment. The DSC data are depicted in Table 2. The onset of melting and peak melting point for the untreated and plasma treated samples were found to lie in the same range. It is worth noting that both untreated and plasma treated polypropylene exhibited more or less same percentage of crystallinity. This confirms that bulk properties of polypropylene were not affected by plasma treatment. Increase in crystallinity yield due to decrease in amorphous contribution was reported in CO2 plasma treated polyethylene (Medard, et al., 2002). Unlike polyethylene, in which radicals form cross-links, polypropylene is subjected to degradation due the stability of free radicals in polypropylene (Masuoka et al., 1989). No change in percentage crystallinity was observed indicating no change in bulk properties of plasma treated polypropylene.

Table 2: DSC Data of Untreated and Various Plasma Treated Polypropylene

Polymer	Tm(onset) (°C)	Tm (°C)	ΔHf (J/g)	Xc (%)
PP	119	162	80.23	38.38
Ar-PP	120	161	80.35	38.44
Ar-O2 PP	120	161	80.24	38.39
N2 PP	119	162	80.21	38.37
He PP	120	162	80.25	38.39

Bio-studies

Enhanced cell adhesion and cell viability were observed from the biocompatibility analysis of plasma treated polypropylene. Argon and nitrogen plasma treated polypropylene was found to be the most suitable process gas among the other plasma treatments for enhancing biocompatibility of polypropylene. During plasma treatment common functional groups observed to be attached to the surface including carbonyl and hydroxyl groups enhanced cell adhesion, spreading and cell viability as indicate by their SEM photomicrographs and MTT reduction test. In nitrogen plasma treatment presence of CO, NH2+ and NH+ stretching vibrations are responsible for enhanced cell adhesion. So the presence of amine and amide groups induces protein-surface interaction by hydrogen bonding. Improved blood compatibility was observed to be better with helium plasma treatment for polypropylene which is indicated by its partial thromboplastin time which exhibited 36.72% increase. Nitrogen plasma and argon-oxygen plasma resulted in reduced platelet adhesion to the surface greatly. So it can be said that argon-oxygen and nitrogen plasma in terms of platelet adhesion and helium plasma treatment in terms of partial thromboplastin time as shown in Fig. 3 are better for improved blood compatibility.

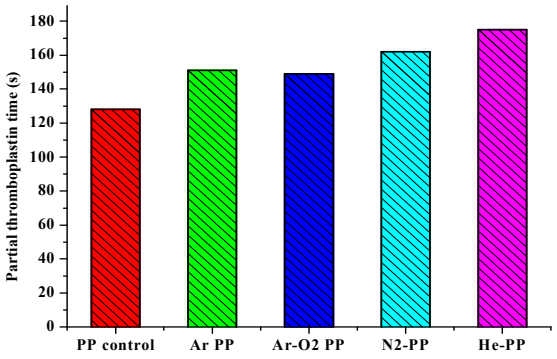

Figure 2. Partial Thromboplastin Time of Untreated and Various Plasma Treated Polypropylene

Conclusion

Polypropylene surface was modified using various plasmas according to the central composite design of response surface methodology to optimize the process conditions. Optimum process conditions were obtained using statistical analysis. Increased surface energy and surface roughness helped in improving hydrophilicity of polypropylene. Various functional groups incorporated to the polymer surface resulted in improved cell adhesion. Biological results prove that surface modification of polypropylene by plasma treatment constitutes a good route towards the improvement of cell adhesion. Prolonged partial thromboplastin time after plasma treatment under optimum conditions indicated improved blood compatibility of treated polymeric surfaces. Better adhesive property was observed with helium plasma treated polypropylene which was indicated by higher peel strength. Argon and nitrogen plasma resulted better biocompatibility while helium and nitrogen resulted better blood compatibility among various plasma treatment.

Reference

1. Egitto, F. D., Vukanovic, V., Taylor, G. N., 1990. Plasma deposition, treatment, and etching of polymers. Eds. R d'Agostino (Boston: Academic) 321–422.
2. Gomathi N., Sureshkumar A., and Neogi S., (2008). RF plasma treated polymers for biomedical applications. Current Science, 94 (11) 1478-1486.
3. Masuoka, T., Hirasa, O., Suda, Y., Ohnishi, M., 1989. Plasma surface graft of n,n-dimethylacrylamide onto porous polypropylene membrane, Radiation physics and chemistry 33, 421-427.
4. Medard, N., Soutif, J. C., Epaillard, F. P., 2002. Characterization of CO2 plasma-treated polyethylene surface bearing carboxylic groups, Surface and coatings technology 160, 197–205.
5. Owens, D. K., R. C. Wendt, 1969. Estimation of the surface free energy of polymers. Journal of applied polymer science 13, 1741-1747.
6. Wu, S., 1982. Polymer interface and adhesion. USA. Marcel Dekker Inc.