

**Research Article**

Investigation on the Bio-degradability of the Starch Modified Polypropylene with the Help of Maleic Anhydride as a Coupling Agent

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Abstract

Polypropylene was modified with starch in 1/20 ratio by adding a coupling agent in the absence and presence of a compatibilizer so as to produce a modified polypropylene with the advantage of bio-degradability in lesser time as compare to normal time span of degradation. As polypropylene a hydrophobic material and starch a hydrophilic material, so maleic anhydride was used as a coupling agent and PVA used as a compatibilizer to produce proper formation of bond. For the proper inter-mixing of the polymers they were swollen by aromatic compound such as toluene at elevated temperature. The material produced was tested in IR spectroscopy, universal testing machine, water absorption test, soil burial test and scanning electron microscopy for the checking of proper inter-mixing, change in mechanical properties and to check the bio-degradability respectively.

Keywords: biodegradable; composite; PVA; soil

Academic Editor: Taihong Shi, PhD, Sun Yat-sen University, China

Received: June 30, 2015; **Accepted:** July 29, 2015; **Published:** August 17, 2015

Competing Interests: The authors have declared that no competing interests exist.

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1. Introduction

Plastics are widely used in every field due to its excellent properties, easy availability, easy molding and cheap price. It is estimated that all over the world near about 140 million tons of polymers are produced synthetically to replace conventional material [1-2]. Over 70% of post-consumer plastic waste is recycled every year which is produced by households and after every recycling their properties reduced and after some cycles they are unable to recycle. Plastics are compounded to resist the environmental degradation and also more cost effective than other conventional materials in terms of manufacturing cost and energy required. Due to these reasons, plastics which are continuously entering in to the waste stream becoming a great problem in the case of pollution. This continuous increasing of waste plastic has led to the increase volume of plastic waste in the landfill which is used to be one of the main methods for the disposal and is now diminishing due to this continuous hike every year. Reduce, reuse and recycle have become substitutes to overcome the problem of increasing waste but all this have their own limitations. Lastly, the plastics will terminate at the landfill again. Plastics have high volume of solid waste and in these field Bio-degradable polymers can play a significant role [3-16].

To reduce the increasing environment issues related to polymers the society has directed its research onto bio-degradable polymers. Polymers, which in natural environment start reducing its chemical properties, mechanical properties and structural properties and finally changes into other smaller compositions which are innocuous in nature. Bio-degradable polymers are usually manufactured by renewable resources which are mostly in the form of starch and cellulose. These bio-polymers are disposed in a bio-waste collection and finally composted which will ultimately reduce into environmental friendly by-products.

Chemical and physical properties of plastic equally affect the process of bio-degradation. The surface condition, first order structure and high order structure all play a significant role in the bio-degradation process of polymer. Surface area, hydrophobic and hydrophilic properties which play a major role, as a hydrophilic polymer of a greater surface area will reduce faster as compare to lower surface area and hydrophilic polymer will reduce in a longer time in presence of water. Chemical structure, molecular weight and molecular weight distribution are the first order structure properties which play a major role as a high molecular weight will take more time in reduction as compare to a low molecular weight. Glass transition temperature, melting temperature, modulus of elasticity and crystallinity are the high order structure properties and they equally affect the biodegradability. Molecular weight and crystallinity are the two most significant properties which affect the bio-degradability criteria the most as other properties are dependent on it. A high molecular weight and crystalline polymer will have a properly packed structure which cannot be easily break by the enzymes and it will be more resistant to degradation as compare to the amorphous one [17-28]. In the present work we have tried to increase the biodegradability of polypropylene by using natural polymer starch along with maleic anhydride and PVA.

2. Experimental Method

2.1 Materials Involved

The Polypropylene pallets were obtained from Indian Oil Corporation Limited, India. The sago starch and polyvinyl alcohol were obtained from the MERCK and SISCO Research Laboratories. Toluene, maleic anhydride and benzoyl peroxide were obtained from CDH Laboratories.

2.2 Instrumentation

FTIR were recorded on Nicolet 380. Mechanical Tests were performed on Instron 3369 Universal Testing Machine and SEM were recorded on the Hitachi 3700 N.

2.3 Preparation of samples

Firstly, the maleic anhydride was added in the toluene in the presence of benzoylperoxide. To this polypropylene pallets, PVA and starch were added at elevated temperature. Resulting solution was then refluxed. These samples were poured on flat container in air for the removal of volatile gases/solvent present in it and collected for the testing. Details of the prepared samples are given in Table 1.

Table 1 Composition of different samples in observation

S. No.	Polypropylene (gm)	Starch (gm)	Polyvinyl alcohol (gm)	Maleic Anhydride (gm)	Benzoylperoxide (gm)	Toluene (ml)
Sample 1	200	0	0	0	0	0
Sample 2	200	10	10	10	1	200
Sample 3	200	10	0	10	1	200

2.4 Measurement and Characterization Techniques

Mechanical strength of the samples were carried out on UTM Instron 3369 machine. In this test material can be tested for the tensile, compression or shear strength as per the requirement. Samples are tested over a high range of load up to the specimen will not break. Samples were prepared by the use of hand injection molding machine. Water absorption test is a simple test to check the change in weight and other surface properties of a material over a limited period of time in the presence of water. In this method simply the change in weight and color are recorded over a period of time. The data collected can be used to determine the different property changes in material. Soil burial test is a simple test to check the change in weight and other surface properties of a material over a limited period of time in the presence of soil. In this method simply the change in weight and color are recorded over a period of time. The data collected can be used to determine the different property changes in material like biodegradability. Fourier Transform Infrared Spectroscopy (FTIR) FTIR analysis is a simple method for the analysis of both the organic and inorganic samples. It can be used in the analysis of the solid, liquid and gases. The samples are analyzed for the presence of the functional groups. The FTIR spectra of all

the samples were carried out on FTIR spectrophotometer (Thermoscientific Nicolet, Model 380) using KBr pressed pellets. Scanning electron microscopy (SEM) is an important tool to analyze the morphology of the samples. This was carried out on Hitachi S-3700N.

3. Results and Discussion

3.1 Mechanical Testing

The samples were tested on the Instiron 3369 Universal Testing Machine. Dumb bell shaped specimens were prepared by hand injection molding to check the change in strength. It was observed that the samples show less ductility and toughness as compare to the pure polypropylene which is due to the presence of starch as it is a brittle material in nature and reduce ductility and toughness when added in to the polymer for the purpose of modification in properties as shown in Figure 1.

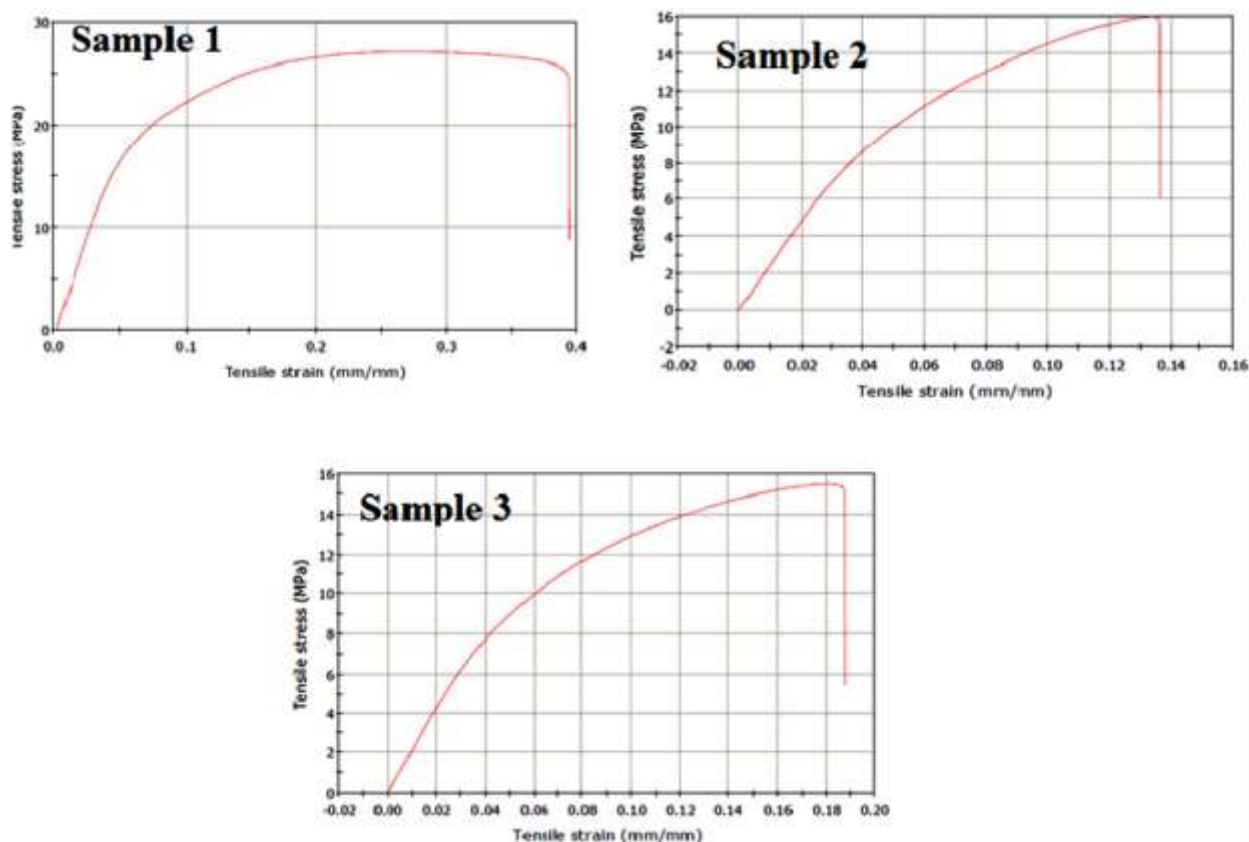


Figure 1 Mechanical strength of samples 1, 2 & 3 shown

3.2 Water Absorption Test

The samples were put in water for 40 days to observe the change in weight as well as size of sample. Observations are recorded in Table 2. It was observed that the samples weight decreases with time in presence of water and polymer particles are dissociating in the water which is due to the bleeding and blooming phenomena as PVA and starch is coming out from the sample in to the water as it shows high affinity to the water as compare to polypropylene and can be seen in Figure 2 [29].

Table 2 Water absorption of samples 1, 2 and 3 with time.

Time (in days)	Sample 1	Sample 2	Sample 3
	Weight in gm		
0	12.6904	13.3593	12.5821
10	12.7061	13.3586	12.4453
20	12.7128	13.2371	12.3112
30	12.7167	13.2087	12.2686
40	12.7189	13.1753	12.1983

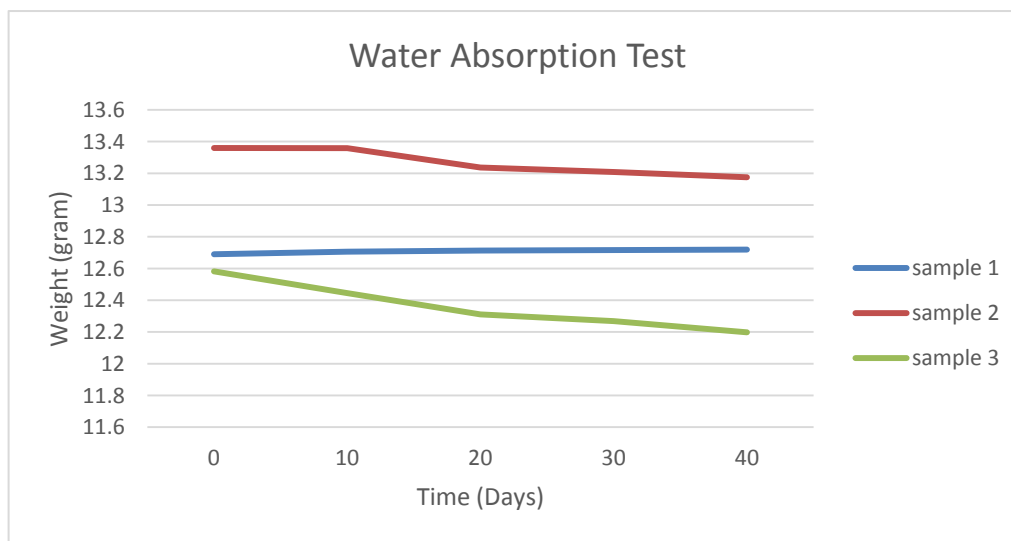


Figure 2 Water absorption behavior of samples 1, 2 & 3 with time.

3.3 Soil Burial Test

In this test, samples were deeply buried in the soil for 40 days to observe the change in weight and are shown in Table 3. It was observed that the sample weight increases with time which may be due to the absorbance of moisture by different materials present in the sample as polypropylene itself a hygroscopic material and whereas starch and maleic anhydride were also able to absorb a great amount of moisture [30].

Table 3 Change in weight of samples before and after performing soil burial test.

Samples	Change in weight (g)	
	Before	After
1	6.3226	6.3235
2	3.5464	3.5669
3	3.8650	3.8872

3.4 Fourier-Transform Infrared Spectroscopy

Fourier-transform spectroscopy was used to collect the qualitative data related to the chemical character and the functional group of the modified polypropylene, starch, maleic anhydride and PVA and their resultant product. The samples were studied under the drift sampling process by Nicolet 380. Figure 3 shows FTIR spectra for sample 1, 2 & 3. The presence of peaks at $2700-3000\text{ cm}^{-1}$, and $800 - 1800\text{ cm}^{-1}$ were the characteristic bands of PP. Sample 2 shows increase in the no. of peaks in between $800 - 1800\text{ cm}^{-1}$ and decrease in the percentage of transmittance at $2700 - 3000\text{ cm}^{-1}$ peaks was typically due to the presence of PVA & maleic anhydride and Starch respectively. Sample 3 shows increase in the no. of peaks in between $800 - 1800\text{ cm}^{-1}$ and decrease in the percentage of transmittance at $2700 - 3000\text{ cm}^{-1}$ and $800 - 1800\text{ cm}^{-1}$ peaks was typically due to the presence of Maleic anhydride and Starch respectively. These observations confirm the modification in PP.

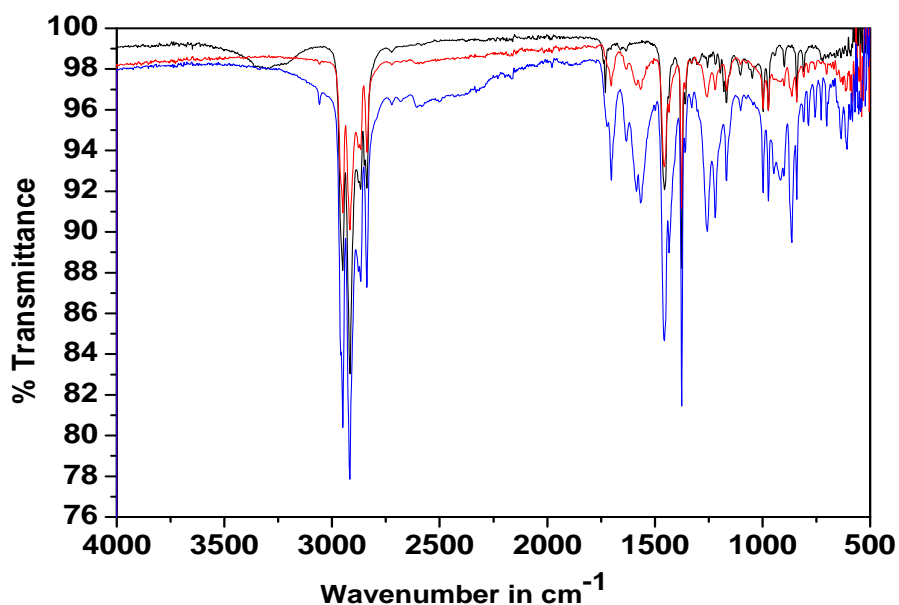


Figure 3 FTIR of samples 1(black), 2(red) &3(blue).

3.5 Scanning Electron Microscopy

The surface morphology of the solid sheet type samples which passed through 40 days of water absorption test and 40 days of soil burial test were analyzed by the help of scanning electron microscope (SEM) and are shown in Figure 4 and Figure 5, respectively. . The samples studied at 15kV with proper magnification in Hitachi 3700 N. The surface morphology of the sample 1 in both the cases of soil burial test and water absorption test shows regular surface and did not show any signs of degradation as pure PP shows good resistance to bio-degradability. The surface morphology of the sample 2 shows irregular surface and it shows good signs of degradation under the soil burial test whereas less signs of degradation under water absorption test as compare to sample 3 as which may be mainly due to the presence of starch and PVA as starch will try to dissociate in water and PVA will try to bind it which will reduce degradation and in soil burial test PVA may help in the growth of bacteria which may result in increased degradation. The surface morphology of the sample 3 shows irregular surface and it shows good signs of degradation under the water absorption test as compare to sample 2 which may be due to the presence of starch whereas less signs of degradation under soil burial test as compare to sample 2 which may be due to the absence of PVA.

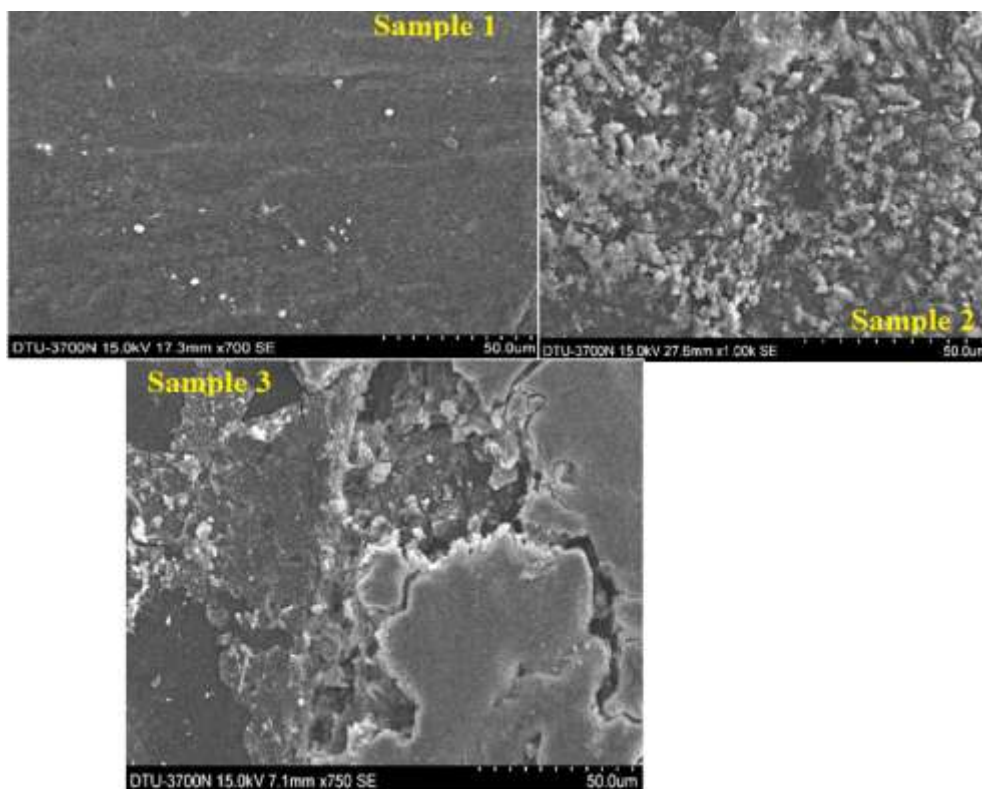
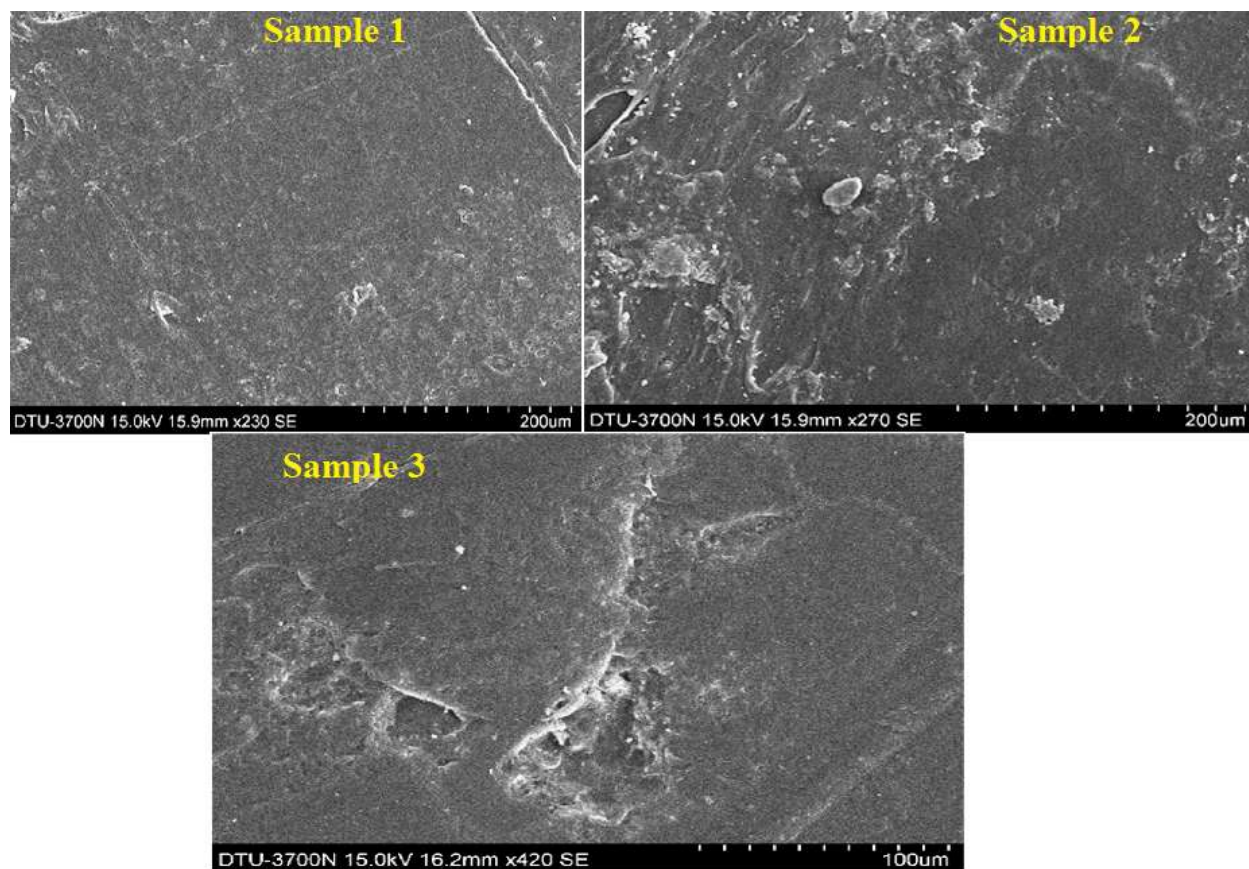


Figure 4 SEM micrograph of samples 1, 2 &3 after 40 days of water absorption test.**Figure 5** SEM micrograph of samples 1, 2 &3 after 40 days of soil burial test.

4. Conclusion

Modified PP samples were synthesized in the presence and absence of the PVA. The samples were first studied on the FTIR spectroscopy for characterization and it was observed that with the incorporation of maleic anhydride as a coupling agent it shows better coupling. The study shows that with the incorporation of the starch in to the polymer reduces its mechanical strength and makes it brittle in nature. These samples were studied for the degradation analysis by 40 days water absorption test and 40 days soil burial test and it was observed that the samples weight decreased in the presence of water and increased in the presence of soil. The same samples which pass through the water absorption test and soil burial test were studied on the SEM and it was observed that the sample in which PVA was added shows less degradation in water absorption test and more degradation in soil burial test as compare to the sample in which PVA is not added. It can be concluded that the modified samples will show less span time for degradation as compare to pure PP and before its commercialization for food packaging articles

and other applications further testing's were required such as degradation testing in different conditions to check out the better environment for degradation , bacteria growth due to the presence of any material present in the food , effect of the addition of different additives on its degradation and mechanical properties and many more.

Acknowledgements

Financial assistance from DTU is greatly acknowledged.

References

1. Pogaku R, Awang B, Christopher C. *Developments in Sustainable Chemical and Bioprocess Technology*. New York Heidelberg Dordrecht, London, **Springer**, 2013
2. Majumda J, Cser F, Jollands MC and Shanks RA. Thermal Properties of polypropylene post-consumer waste (PP PCW). *Journal of Thermal Analysis and Calorimetry*. 2004, 78:849-863
3. Marcilla A, Gomez A, Reyes-Labarta JA and Giner A. *Polymer Degradation Stability*. 2003, 80:233-240
4. Mrkic S, Galic K and Ivankovic M. Effect of Temperature and Mechanical tress on Barrier Properties of Polymeric Films Used for Food Packaging. *Journal of Plastics Film and Sheeting*. 2007, 23:239
5. Arkatkar A, Arutchelvi J, Sudhakar M, Bhaduri S, Uppara PV and Doble M. Approaches to enhance the biodegradation of polyolefins. *The Open Environmental Engineering Journal*. 2009, 2:68-80
6. Gu J-D. Microbiological deterioration and degradation of synthetic polymeric materials: recent research advances. *International Biodeterioration and Biodegradation*. 2003, 52:69-91
7. Albertsson AC and Karlsson, S. Aspects of biodeterioration of inert and degradable polymers. *International Biodeterioration and Biodegradation*. 1993, 31:161-170
8. Ogier L, Rabello MS and White JR. Influence of morphology and surface preparation on the weatherability of polypropylene. *Journal of Materials Science*. 1995, 30(29):2364-2376
9. Severine F, Gallo R and Ipsale S, Some aspects of the environmental photo-degradation of LDPE. *Polymer Degradation Stability*. 1998, 22(1):53-61
10. Billingham NC and Calved PD. *An Introduction- Degradation and Stabilization of Polyolefins*. London: Aplied Science Publishers, 1983
11. Hinsken H, Moss S, Pauquet JR and Zweifel H. Degradation of polyolefins during melt processing. *Polymer Degradation Stability*. 1991, 34(1-3):279-293
12. Kelen T. *Polymer Degradation*. Van nostrad Reinhold. New York: United States, 1983.
13. Whiteley KS, Heggs TG, Koch H and Mawer RL. Polyolefins. In: *Ullmann's Encyclopedia of Industrial Chemistry*. New York: **Elsevier's, VCH**, 1982. 487 p
14. Canevarolo SV. Chain scission distribution function for polypropylene degradation during multiple extrusions. *Polymer Degradation and Stability*. 2000, 709:71-76
15. Premraj R and Doble M. Biodegradation of polymers. *Indian Journal of Biotechnology*. 2005, 4:186-193

16. Arutchelvii J, Sudhakar M, Arkatkar A, Doble M, Bhaduri S and Uppara PV. Biodegradation of polyethylene and polypropylene. *Indian Journal of Biotechnology*. 2008, 7:9-22
17. Fleming H-C. Relevance of biofilms for the biodeterioration of surfaces of polymeric materials. *Polymer Degradation and Stability*. 1998, 59:309-315
18. Albertsson AC and Karlsson S. Macromolecular Architecture-Nature as a Model for degradable polymers. *Journal of Macromolecular Science, Part A: Pure Applied Chemistry*. 1996, 33(10):1571-1579
19. Vander Wal A, Mulder JJ and Gaymans RJ. Fracture of polypropylene: 2. The effect of crystallinity. *Polymer*. 1998, 39:5477-5481
20. Sudhakar M, Doble M, Sriyutha MP and Venkatesan R. Marine microbe mediated biodegradation of low and high density polyethylenes. *International Biodeterioration and Biodegradation*. 2008, 61:203-213
21. Sudhakar M, Trishul A, Doble M, Suresh K, Syed J, Umadevi VR et al. Biofouling and biodegradation of polyolefins in ocean waters. *Polymer Degradation and Stability*. 2007, 92:1743-1752
22. Liang CY and Pearson FG. Infrared spectra of crystalline and stereoregular polymers. Part I. Polypropylene. *Journal of Molecular Spectroscopy*. 1960, 5:290-306
23. Hoff, Ray and Mathers, Robert T. Handbook of Transition Metal Polymerization Catalysts. *John Wiley & Sons*. 2010, pp. 158
24. Moore, EP. *Polypropylene Handbook. Polymerization, Characterization, Properties, Processing, Applications*, **Hanser Publishers**: New York, 1996
25. Maier, C, Calafut, T. *Polypropylene: the definitive user's guide and databook*. **William Andrew**. p. 14, 1998
26. Manfred L. Polyvinyl Compounds and Others. In: *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim, **Wiley-VCH**, 2000
27. Fromageau, J, Brusseau, E, Vray, D, Gimenez, G, Delachartre, P. Characterization of PVA cryogel for intravascular ultrasound elasticity imaging. *IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control*. 2003, 50(10): 1318 - 1324
28. Kurt L, Herbert H, Werner F, Norbert F. Maleic and Fumaric Acids. In *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: **Wiley-VCH**;2005
29. Brydson JA. *Plastics Material*. **Butterworth Heinemann**. 7th Edition, 1999, p124-150
30. Ohtake, Y, Kobayashi, T, Asabe, H, Murakami, N and Nono, K. Oxidative Degradation and Molecular Weight Change of LDPE Buried under Bioactive Soil for 32-37 Years. *Journal of Applied Polymer Science*. 1998, 70: 1643-1659