A

Dissertation Report

On

"To reduce oxygen Transmission rate of plain bi-axially oriented poly propylene film for flexible packaging of food products"

Submitted By

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Under the Supervision of

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CANDIDATE'S DECLARATION

I hereby, declare that the work, which is being presented in this end term dissertation report, entitled "***To reduce oxygen Transmission rate of plain bi-axially oriented poly propylene film for flexible packaging of food products***" was carried out by me during the period June 2018-May 2019 as a part of the partial fulfilment of my M. Tech dissertation, under the supervision of **Dr. Anurag Kulshreshtha,** *Adjunct faculty, Department of Paper Technology, Indian Institute of Technology Roorkee***.** The matter embodied in this dissertation report has not been submitted by me for the award of any other degree in any other institute.

Date: Amit Suhag

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ACKNOWLEDGMENT

A dissertation is not only an accomplishment but also one of the achievements in life. The satisfaction and satiety of overcoming the hurdles faced during the research work cannot attained without expressing sincere gratitude to all those who guided and supported me during the entire course of work

I am deeply indebted to my supervisor **Dr. Anurag kulshreshtha** (Adjunct faculty, Department of Paper Technology, IIT Roorkee) and for inspiring me to enhance my knowledge by pursuing the innovative area of my dissertation work "***To reduce oxygen Transmission rate of plain bi-axially oriented poly propylene film for flexible packaging of food products***". Their skill, full guidance and deep knowledge of the subject made the interpretation of seemingly difficult work look easy.

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Amit Suhag

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ABSTRACT

This thesis report is based on research work on oxygen barrier property of plain BOPP film. Research work is done to reduce the oxygen transmission rate of plain BOPP film. Reduction in oxygen transmission rate of plain BOPP is important for flexible food packaging. It results in increase in shelf life of food product for example bread. To reduce OTR value coating of a hybrid solution is applied on the BOPP film. Coating is done by two different methods, cylinder coating and dispersion coating.

In this research work a hybrid solution (with different composition) is prepared by mixing an organic component and an inorganic component. Tetraethoxysilane (TEOS) is used as inorganic component and poly vinyl alcohol is used as organic component. Corona treated plain BOPP film is coated with these prepared solutions. OTR value of this coated film was measured by appropriate apparatus. This coated film is characterized by FTIR, FE-SEM, TGA and DSC.

Then application of this experiment is performed by packaging of bread in pouches formed by impulse sealing. These pouches are made of coated BOPP film with different composition solution. A reference sample is also prepared, packaging of bread in pouch made of plain BOPP without coating. Then results are compared.

Contents

LIST OF FIGURES

NOMENCLATURE

TEOS- Tetraethoxysilane

PVA- Poly vinyl alcohol

TGA- Thermo gravimetric analysis

DSC- Differential scanning calorimetry

FTIR- Fourier transform infrared spectroscopy

OTR- Oxygen transmission rate

CHAPTER-1

INTRODUCTION

In contrast to glass and metal packaging, a plastic packaging is permeable to various gases, water vapour, and organic vapour and to other low molecular weight compounds like aromas, flavour, and additives present into food. Degree of permeation may be different depending on properties of different plastic. Different polymers are used in food packaging industry depending on the properties of food. Selection of correct packaging material is important to increase the shelf life of food product. For example, spoilage mechanisms in bakery products like bread are mould growth and moisture migration. Moulds are aerobic micro-organisms, so by providing barrier to oxygen through a packaging material we can prevent growth of moulds. Similarly we can select appropriate polymer film to provide moisture barrier.

1.1 Role of package in food packaging:

- One of the roles of packaging is to protect the food from environment and other factors till the final consumption of food. Package should provide the sufficient barrier against harmful substances.
- Another role of package can be to provide convenience for transport of product.

Packaging acts as a silent salesman to the product. So, it also helps in marketing of product. It also provides information about product to the consumer. So, printability and optical properties of packaging material are important factor to decide the packaging material. BOPP films have excellent clarity, transparency and gloss.

1.2 Properties of BOPP films:

- Density (0.9g/cc) of BOPP is lowest of all common packaging materials.
- As a result of biaxial orienting process, mechanical strength, dimensional stability, stiffness, optical properties and barrier properties are improved as compared to normal PP films.
- Low tear resistance make it suitable for easy-open applications.
- BOPP films have excellent gloss and high transparency that give it an excellent look and fine finish.

- BOPP films provide good barrier to moisture as shown in fig-1 and BOPP films provide resistance against outside pollution or dust particles while other polyester films are not resistant to outside pollution.

1.3 Comparison of barrier properties of different polymers:

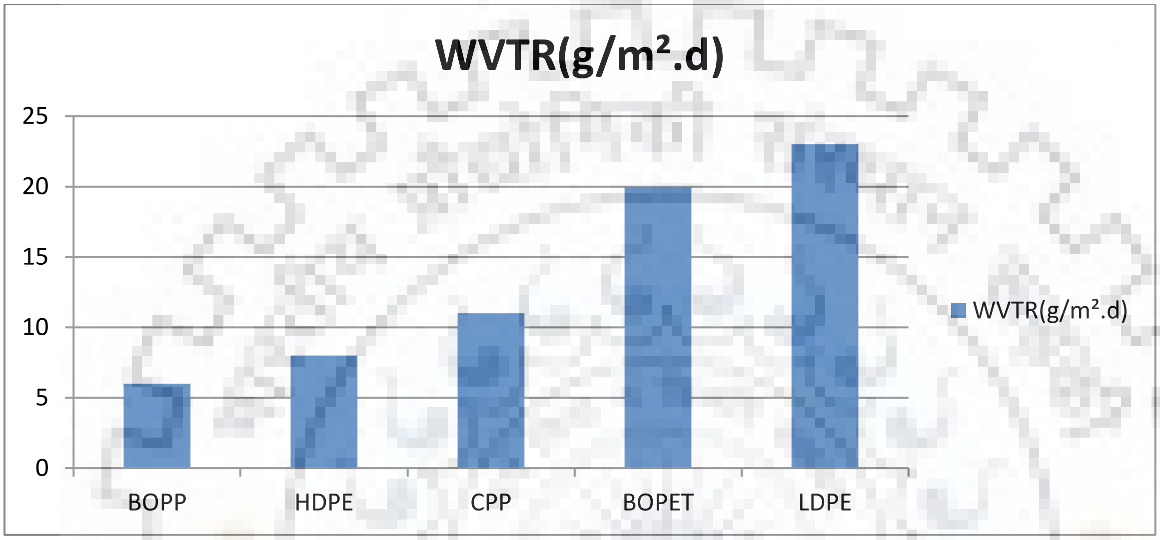


Figure 1 barrier property (water vapour transmission rate)

BOPP has exceptional moisture barrier as compared to other polymeric packaging films.

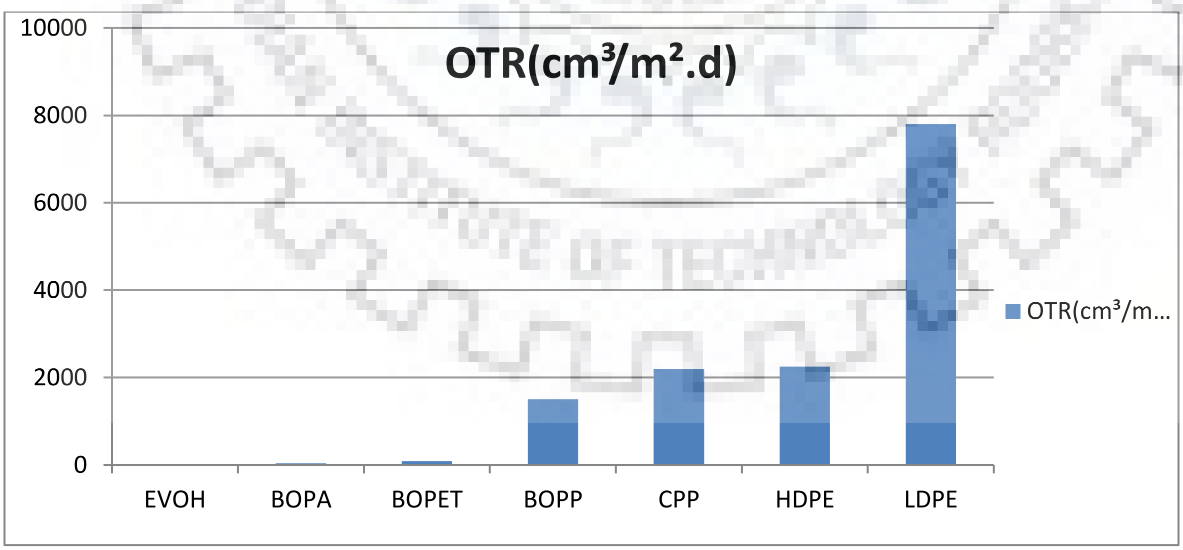


Figure 2 oxygen transmission rates of different materials

BOPP has relatively poor OTR value.

Oxygen transmission rate of BOPP can be reduced by coating of some barrier materials. Apart from the material used for barrier, coating method is also important to reduce OTR value. Engraved cylinder coating and dispersion coating is used in this research work.

1.4 Gravure cylinder coating:

Gravure coating is a practice which is used for coating of fluids with various viscosities on a substrate. Coat thickness can be varied in range of 1 micron up to 50 microns. Application of gravure cylinder coating is increasing in various market sectors.

It differs from other coating techniques because in this technique one roll is having engraved surface (gravure pattern). Both shape and size of gravure pattern can be varied.

Depending on distinct gravure coating arrangements this technique can be divided into two types:

- Direct gravure coating
- Offset gravure coating

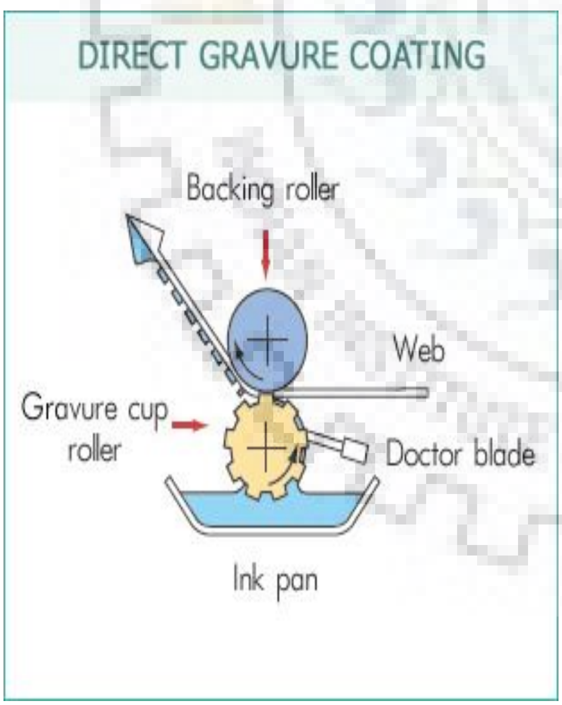


Figure 4 Direct gravure coating

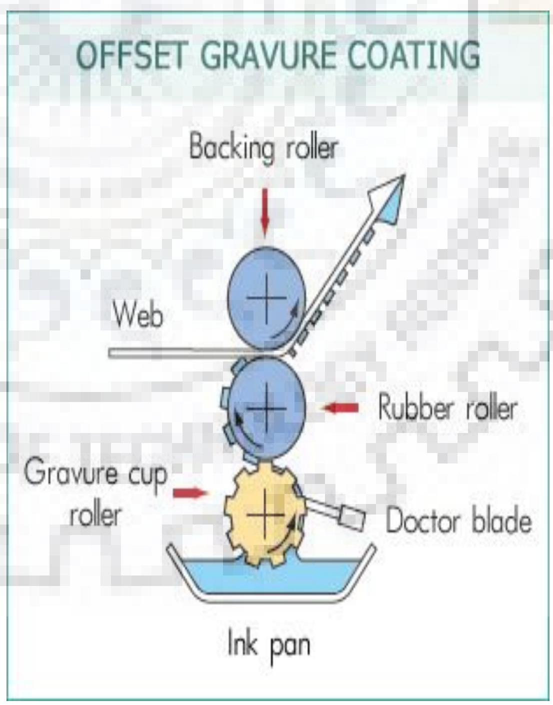


Figure 3 Offset gravure coating

Gravure cell specification:

Specifying the gravure cell is important in the gravure coating process. Shape and size of cell define the operability of coating process.

Fig 3 shows different shape of cell used on engraved cylinder surface.

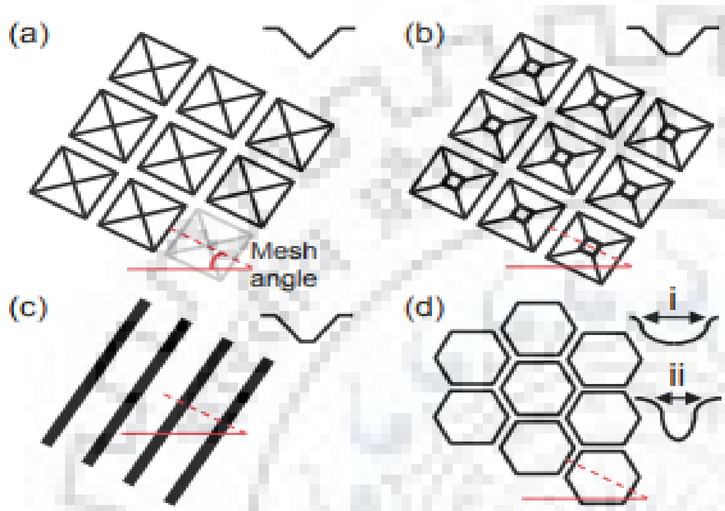


Figure 5 (a) pyramidal, (b) quadrangular, (c) continuous tri helical, (d) laser engraved ceramic cells.

CHAPTER-2

LITERATURE SURVEY

2.1 paper-1: S. Amberg-schwab, et al. "Inorganic-Organic Polymers with Barrier Properties for Water Vapor, Oxygen and Flavors", 1998, 141-146

With inorganic-organic polymers a coating solution is prepared to provide barrier for water vapour, oxygen and aroma components.

System consisted of the following starting materials: tetramethoxysilane, zirconium propoxide, aluminum-sec-butylate, 3- glycidoxyproyl-trimethoxysilane and 3-aminopropyltriethoxysilane. After hydrolysis with the stoichiometric amount of water with respect to the hydrolysable alkoxy groups and co-condensation at 15C the solution was stirred for two hours at 25°C. The sol, which had a solid content of 50%, was applied with a spiral applicator and cured for 1 hour at 130°C. The coating thickness was 5 µm

Results-

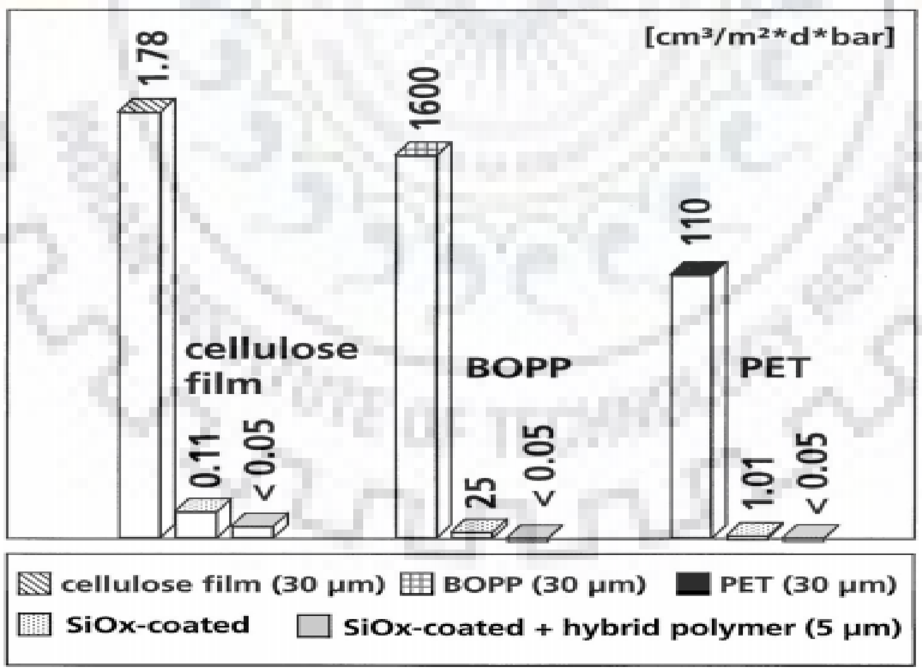


Figure 6- OTR of uncoated and coated regenerated cellulose, BOPP and PET films.

2.2 Paper-2: Roger Bollstrom, Roger Nyqvist, Janet Preston, Pekka Salminen, and Martti Toivakka "Barrier properties created by dispersion coating", 2013, 45-51.

Conclusion: Dispersion coating has received increasing attention as a production method to apply barrier coatings, being hailed as more environmentally friendly compared with extrusion coating or lamination. High barrier properties against gases and liquids are required, and the growing interest for paper to be used as a substrate in functional applications sets new requirements regarding barrier properties against solvents and acids. Barrier properties are affected of type of coating method used. Dispersion coating provide more uniform coating. So barrier properties can be improved by changing the coating method.

2.3 Paper- 3: N. Kapur, R. Hewson, P.A. Sleigh, J.L Summers, H.M. Thompson, S.J. Abbott "A Review of Gravure Coating Systems", 2011, 56-60.

Conclusion: Gravure coating systems and there mechanism are discussed in this paper. It is reflected that gravure coating is a versatile process which is having application in various sectors. Different shapes and size of gravure cells have different effect on barrier coating on a substrate. The basic difference in working of direct gravure coating and offset gravure coating is shown.

2.4 PAPER-4: Tahira Pirzada, Syed Sakhawat Shah "Water-Resistant Poly (vinyl alcohol)-Silica hybrids through Sol-Gel Processing", 2014, 620-626.

Conclusion: The hybrid solution through sol gel processing of mixture of PVA and silica precursor prepared. Ratio of PVA and silica precursor is varied and its effect on the surface structure surface structure, thermal properties, crystallinity and solubility of the hybrids were investigated. PVA is highly water soluble but the hybrid solutions showed considerably reduced water solubility. This behaviour of PVA in the hybrids can be due to the unavailability of –OH group.

2.5 Paper-5: P. Dias, A. Hiltner, E. Baer, J. Van Dun, H. Chen, and S.P. Chum "Structure and properties of bi-axially oriented poly propylene (BOPP)", 2006, 2660-2664.

Conclusion: Mechanical and barrier properties of film are improved by orientation of film. This study of biaxial orientation was undertaken to contrast the effect of chain architecture on stretching conditions and the follow-on properties of bi-axially oriented films. This study compares two isotactic propylene homo-polymers formed with different catalysts in terms of the biaxial orientation process and the resultant properties of the bi-axially oriented films. Phase transitions of BOPP film is analyzed using DSC.

2.6 Paper-6: V.L. Lazića, J. Budinski-Simendića, J.J. Gvozdenović and B. Simendić "Barrier Properties of Coated and Laminated Polyolefin Films for Food Packaging" , 2010, 855-858.

The demand of food industry is for the polymeric films which can provide specific barrier to penetration of gases, moisture and aroma. The aim of this study was to find out differences between barrier properties of coated and uncoated poly olefins films.

Conclusion: Results of this study shows that lamination process strongly influenced the gas permeability of film. It is found that metalized BOPP has excellent barrier properties and it can be used to over wrap the food products.

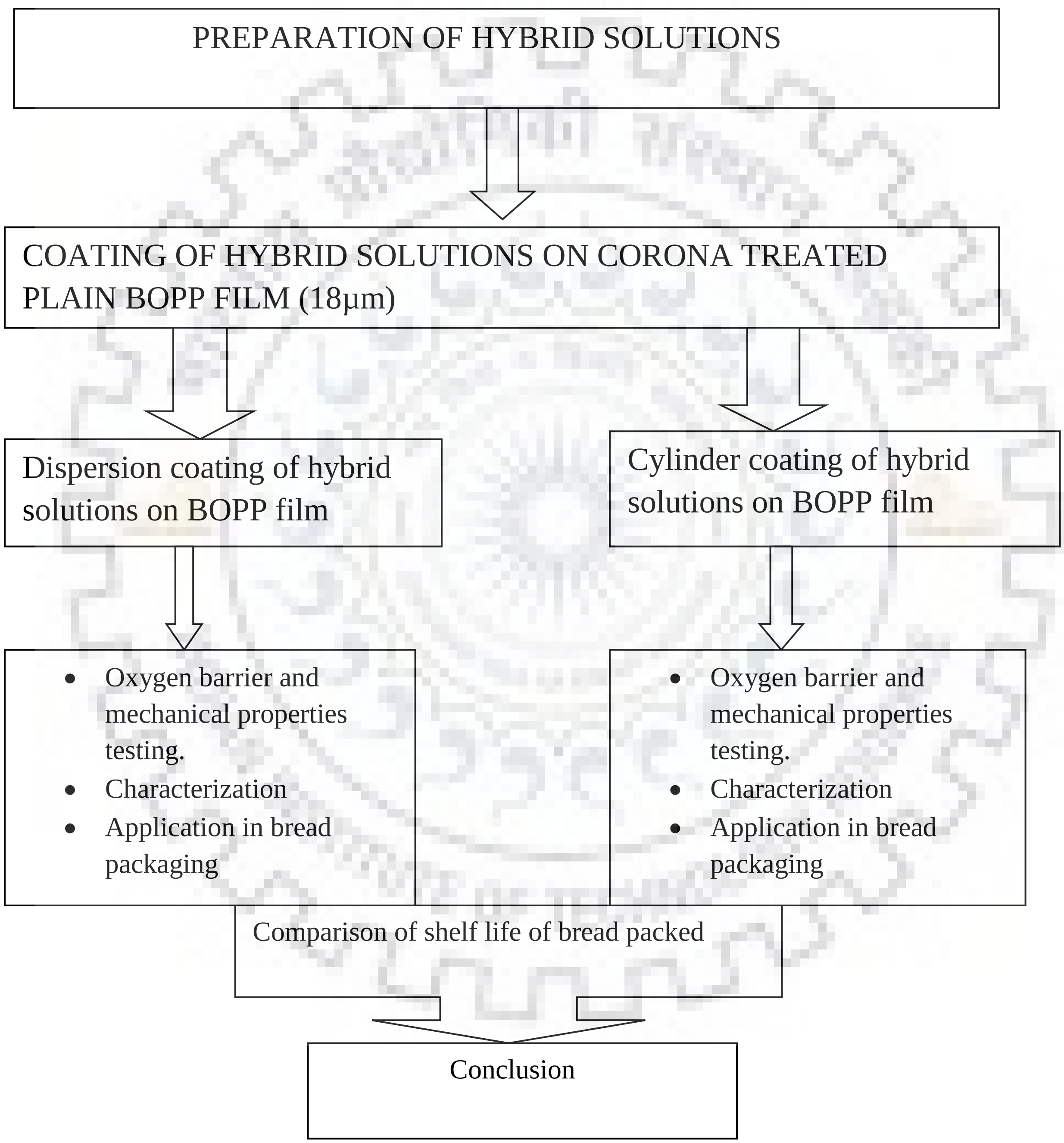
For preservation of vegetables in modified atmosphere, permeability of CO_2, O_2 and N_2 molecules should be minimize through the packaging material. So, multilayer high barrier foils can be used. It was found that lamination process improves the oxygen barrier of film but it is not necessary that it will also improve moisture barrier of the film.

2.7 Paper-7: Food Packaging Permeability Behaviour: A Report Valentina Siracusa, 2012, 1-11.

Conclusion: Generally experiments are carried out in temperature range of 20°C to 60°C. These are the temperatures under which food can be subjected. So, it is important to have data of permeability under these temperatures. Knowledge about the interaction of food and packaging is also very important. Relative humidity greatly affects the permeability in case of poly olefins.

CHAPTURE-3

METHODOLOGY



CHAPTER-4

MATERIAL AND METHOD

4.1 Coating of organic-inorganic hybrid solution on plain BOPP film

4.1.1 Materials

Reagents used are Tetraethyl orthosilicate, formally known as Tetraethoxysilane (TEOS) as inorganic component, poly vinyl alcohol (PVA) as organic component, ethyl alcohol. Distilled water is used to prepare these solutions.

4.1.2 Experimental procedure

A mixture is obtained by mixing TEOS, distilled water and ethyl alcohol. This mixture is stirred for 1 hour at room temperature to get partially hydrolyzed TEOS solution under acid catalyst (HCL) to control Ph. The molar ratio of TEOS: Ethyl alcohol: water is taken as 1:2:2. Different partially hydrolyzed silica solution is prepared with TEOS content of 0.02, 0.04 and 0.05 mol.

A separate polymer solution is prepared by dissolving 2 gm of PVA powder in 20 ml distilled water.

This PVA solution is then mixed with partially hydrolyzed silica sol. This PVA solution is mixed with different composition silica solution. Then the mixture is stirred for 2 hour at room temperature to produce hybrid coating solution to coat on BOPP film.

Then this solution is used for coating on corona treated plain BOPP film of thickness 18μm. Corona treatment is done to increase the surface energy of BOPP film surface. Coating is done by two different methods:

- Engraved cylinder coating
- Dispersion coating

In cylinder coating BOPP film is doubled coated to have uniform coating. After coating, these hybrid coated films are dried by blowing air. After that oxygen transmission rate and other properties of these films coated with hybrid solution is tested.

Then 3-side seal pouches are made with plain BOPP film and coated BOPP film. Pouches are made with the help of impulse sealer. Bread pieces are packed in those pouches. Then these samples are stored at room temperature and in controlled temperature. Then shelf-life of different samples compared with reference sample. Reference sample is bread packed in pouch made of plain BOPP film (uncoated).

Figure 7 hybrid solution prepared.

Impulse sealer:

Heated sealing wires are used in impulse heat sealers which are activated when sealing bar is hard-pressed close. Silicone seal pad is used to make sealing bar because it is able to bear up direct heat contact. The sealing bar presses on the wire and film to melt and mend the material, forming a seal. flat sealing wire make stronger and thicker seals. Round wire sealer make thinner and less visible seal.

The heat element is triggered:

Figure 8 sealing bar is closed with film in between.

When sealing bar is closed, a micro switch is enacted and electrical current is sent to the end connector posts. End posts heat up the sealing wire with electrical current. The micro switch also activated the sealing light to point out sealing has begun.

Figure 9 sealing begins.

When the micro switch engages, the sealing wire is rapidly heated. Wire is heated and heat evolved by it melts the material which is use. The pressure from the sealing bar being pressed down mends the two sides together creating a seal. Upon finishing point, the seal light will turn off. It shows that the seal is complete.

CHAPTURE-5

RESULT AND DISCUSSION

5.1 Various properties and results:

Table-1

Property		Unit	Method	Corona treated BOPP film (18µm)	BOPP film (Dispersion coated with 0.04 water based adhesive)	BOPP film (Cylinder coated with 0.04 water based adhesive)	BOPP film(cylinder coated with 0.02 water based adhesive)	BOPP film (dispersion coated with 0.05 water based adhesive)
Thickness		Micron	Internal	17.5	18	17.5	18	18
Average GSM		gm/m^2	Internal	17.6	18.6	17.6	18.6	18.6
Haze		%	D-1003	4.9	5.1	5.4	4.5	4.3
COF		static	ASTM D-1894	0.35	0.52	0.48	0.45	0.56
		dynamic		0.4	0.54	0.51	0.47	0.54
Tensile strength	MD	Kg/cm^2	ASTM D--882	1095	1152	1045	1024	975
	CD			2908	3200	3000	2815	2954
% elongation	MD	%		250	306	250	278	301
	CD			63	75	81	75	74
OTR		$cc/m^2/day$	ASTM D-3985	200-400	72	92	200	200-300

These results show the effect of coating on oxygen barrier, mechanical and optical properties of BOPP film. OTR value of BOPP film dispersion coated with hybrid solution containing 0.04 mol TEOS is reduced upto 72 cc/m^2.day.

Comparison of oxygen transmission rate of dispersion coated and cylinder coated film:

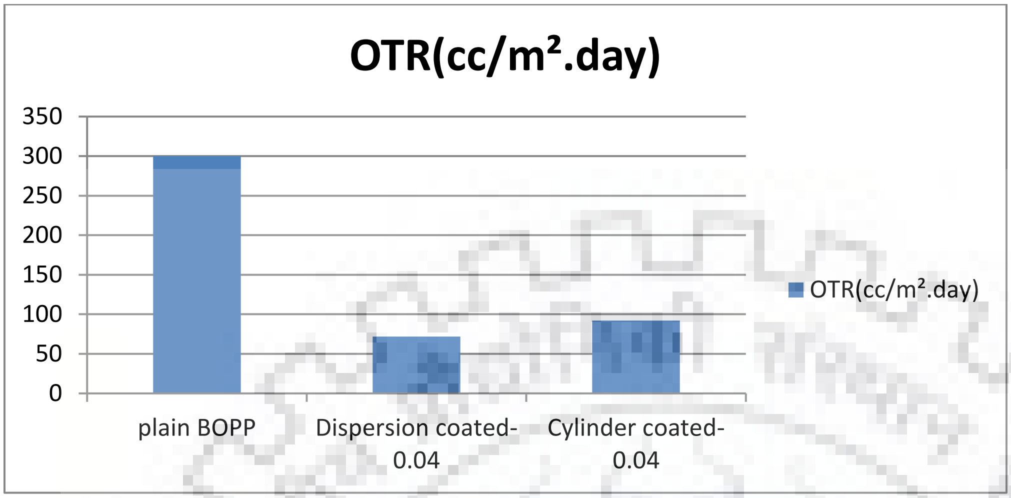


Figure 10-comparison of OTR values.

As can be seen from graph there is significant difference between OTR values of plain BOPP and coated BOPP. Also, significant difference in OTR Values of dispersion coated film and cylinder coated film. Dispersion coated film has greater reduction in OTR value as compared to cylinder coated film.

This difference is because in cylinder coating, hybrid solution is coated through cells engraved in cylinder surface and due to presence of gap between cells there is lack of uniformity in coating. In dispersion coating uniformity of coating on surface is more so there is increase in barrier of oxygen transmission rate.

Comparison of haze value of different sample:

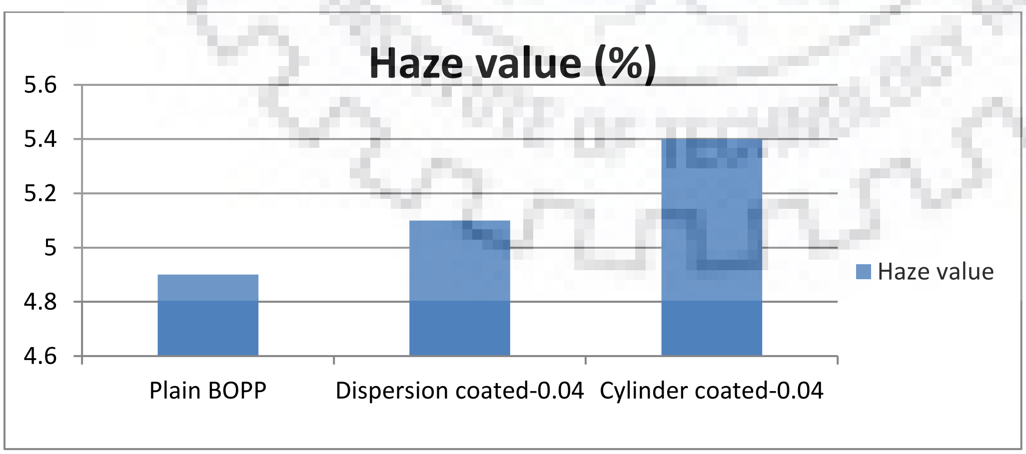
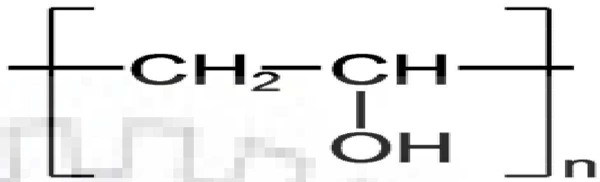


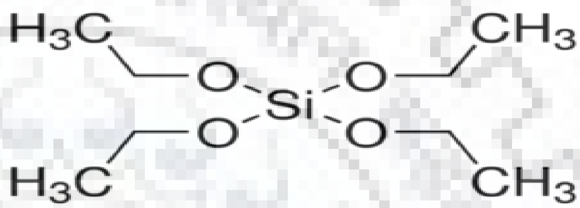
Figure 11 Comparison of haze values.

5.2 Chemistry of hybrid solution:

Poly vinyl alcohol (PVA):

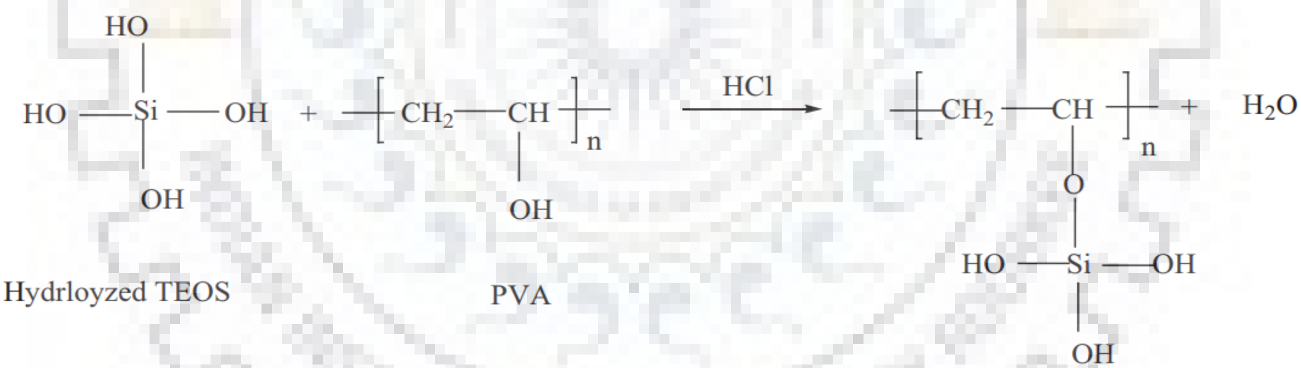


Tetraethoxysilane (TEOS):

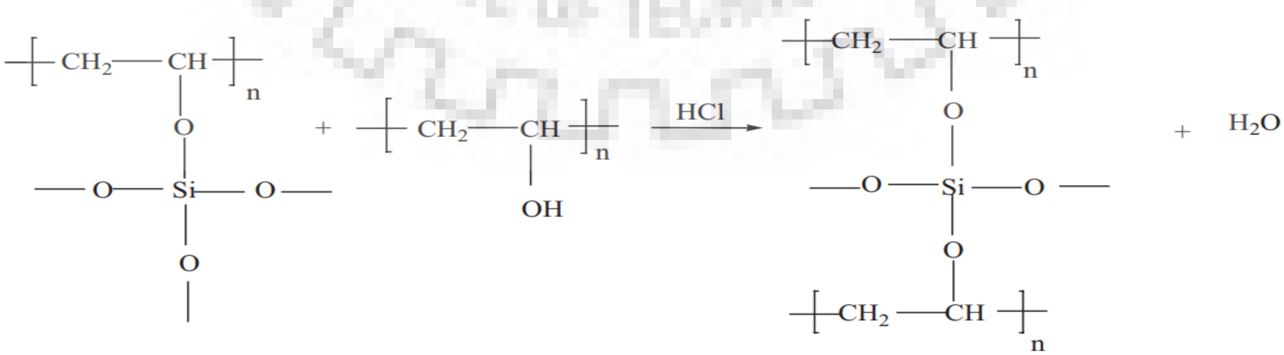


Possible interaction of PVA and TEOS:

Hydrolysis:



Condensation:



5.3 Characterization of coated films:

5.3.1 Fourier Transform Infrared Spectroscopy (FTIR):

FTIR is analytical technique used to recognize organic, polymeric and also inorganic components. In this technique infrared light is used to scan test samples and study chemical properties. The FTIR apparatus sends infrared radiation of about 10,000 to 100 cm^{-1} through a sample, with some radiation absorbed and some passed through. Sample molecules convert absorbed radiation into rotational and vibrational energy. The resulting signal at the detector presents as a spectrum. Each molecule or chemical structure will create a unique spectral fingerprint. IR spectrum can be split into two region:

- 4000-1000 cm^{-1} recognized as functional group section.
- $\leq$1000 cm^{-1} recognized as fingerprint section.(spectra are most complex)

FTIR analysis for hybrid solution with TEOS content of 0.04 mol was performed. The measured spectra is shown in figure-12.

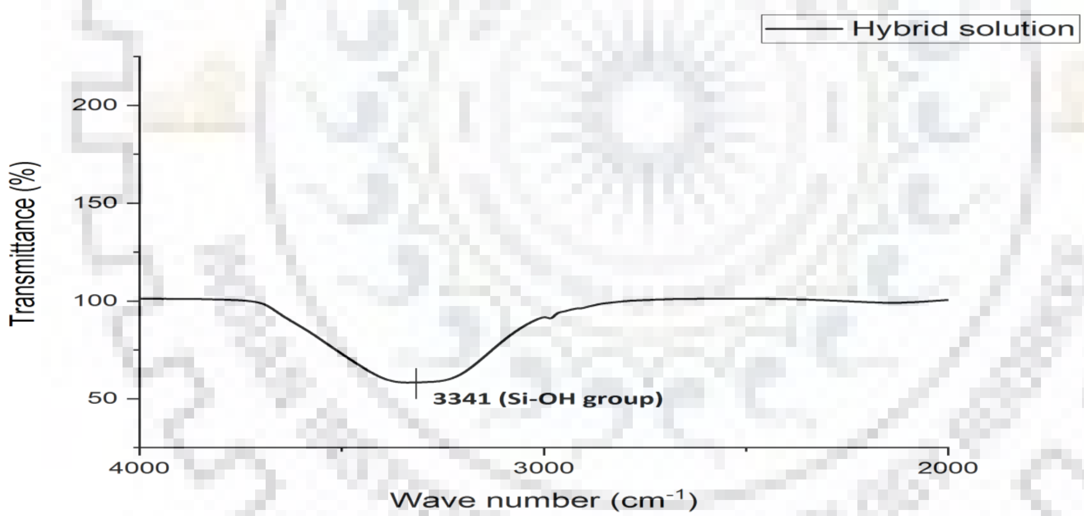


Figure 12- FTIR spectra of hybrid solution with TEOS content 0.04 mol.

Figure 12 shows the peak of hydroxyl group (Si-OH) of hybrid solution. It shows the presence of hydrolyzed TEOS in hybrid solution prepared.

5.3.2 Thermo gravimetric analysis (TGA):

It is a technique of thermal analysis in which mass of sample is considered over time with change in temperature. TGA can be used to check thermal stability of a material. If there is no change in mass of sample over a desired temperature range then the species is thermally stable. TGA give upper use temperature of a material. After this temperature material starts to deteriorate.

In this analysis temperature range is set from room temperature to 800°C at heating rate of 10°C per min under N_2 atmosphere with a flow rate of 200 ml per minute.

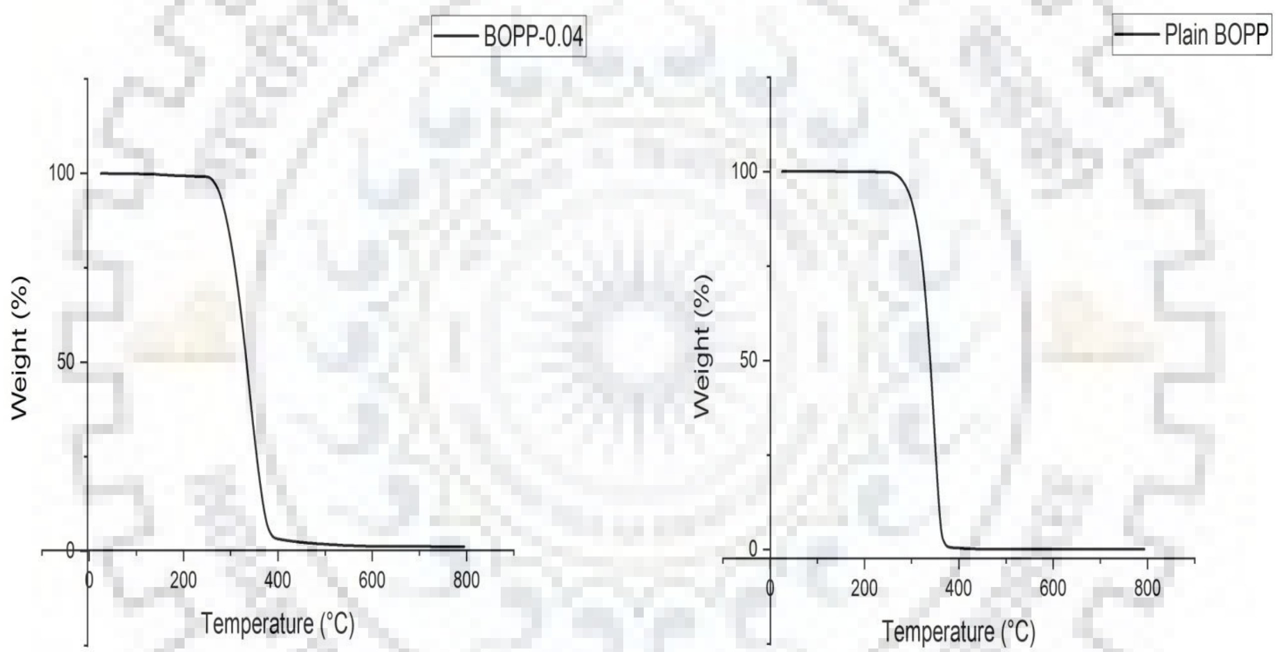


Figure 13-Graph representing TGA data analysis of plain BOPP film and BOPP coated with 0.04 coating adhesive.

Comparison of TGA result:

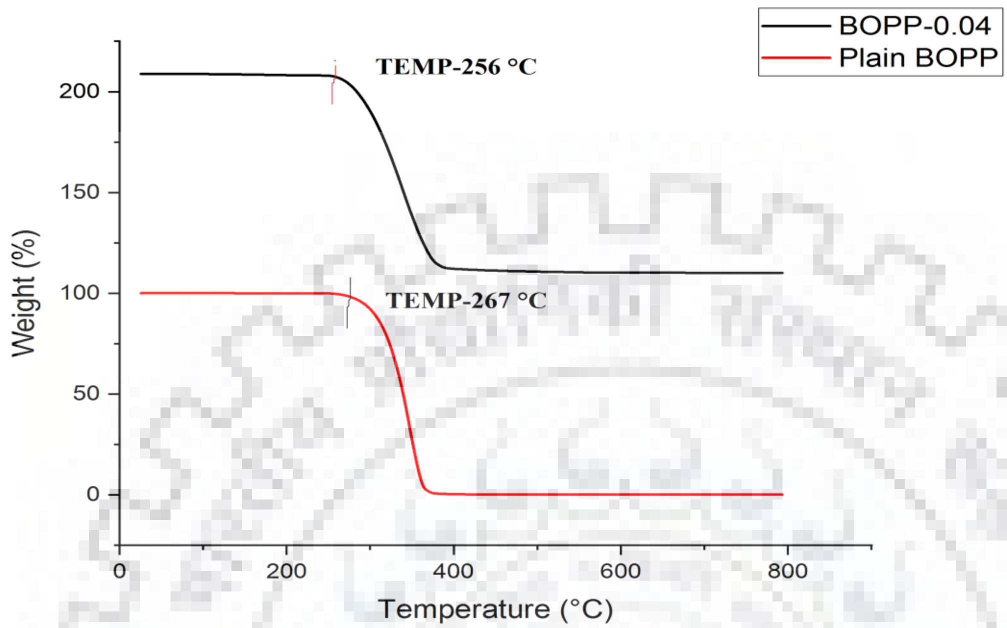


Figure 14- Stacked graph of TGA analysis of plain and coated BOPP.

TGA results of plain BOPP shows there is no loss of weight until the temperature raises to 256°C. So, material is thermally stable up to this temperature. After this temperature plain BOPP start to decompose.

This temperature is called starting of decomposition temperature. While coated BOPP film shows no loss in weight until 267°C. It means coated BOPP is thermally stable up to this temperature and after this temperature material start to decompose. It is clear from the graph that thermal stability of coated BOPP decreases. Material decomposition continues until 373°C temperature in case of plain BOPP. While material decomposition completed at temperature of 390°C in case of coated BOPP film.

5.3.3 Differential scanning calorimetry (DSC):

DSC is a thermo-analytical method in which the differences in the amount of heat necessary to increase the temperature of a sample and reference are calculated as a function of temperature. Sample and reference are maintained at nearly same temperature during the testing. Heat capacity of reference sample should be well known over the temperature ranges to be analyzed. The DSC analysis is used to study phase transitions such as glass transitions, melting point, or exothermic decomposition.

This analysis is done in temperature range of -70°C to 180°C at heating rate of 5°C per min and cooling rate of 5°C per min with N_2 atmosphere flow rate 200 ml per min. Temperature of sample holder increases linearly as a function of time.

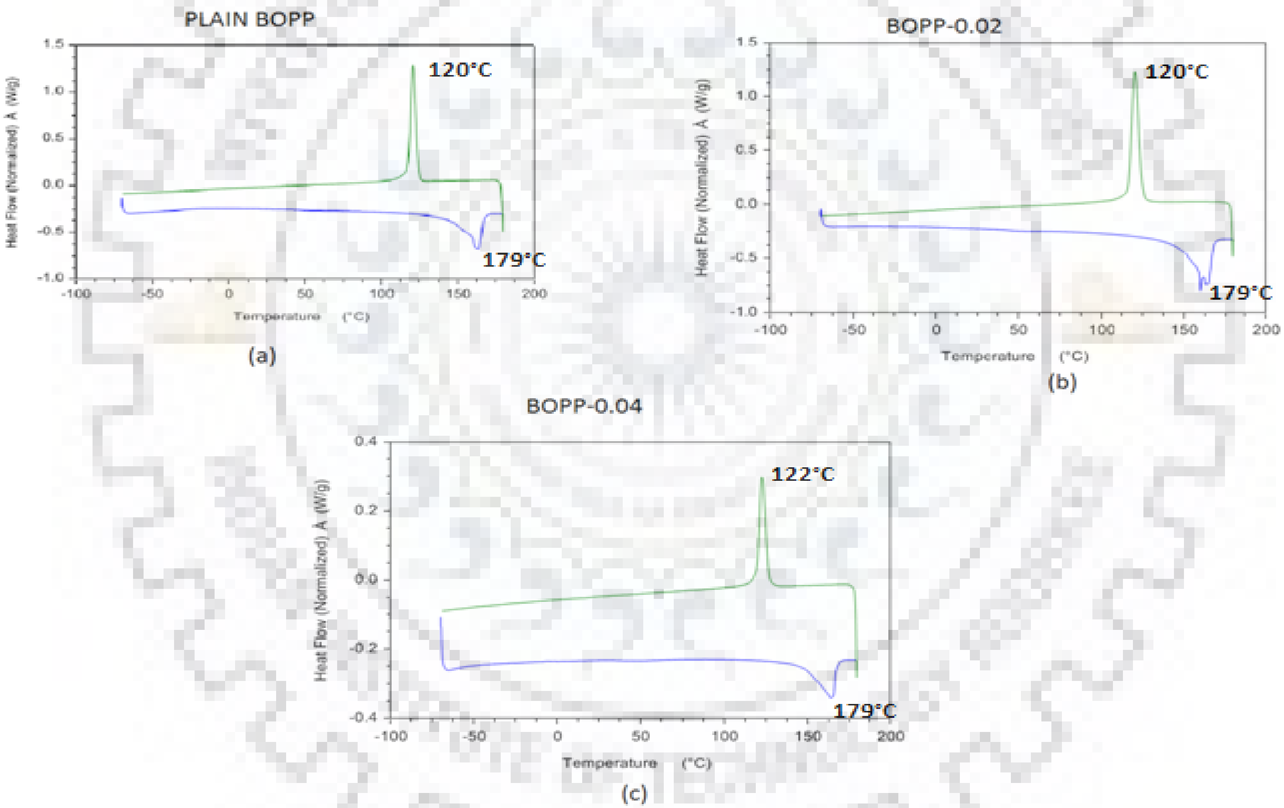


Figure 15- (a)- DSC analysis of plain BOPP film, (b)- DSC analysis of BOPP film coated with hybrid solution having 0.02 mol TEOS cntent, (c)- DSC analysis of BOPP film coated with hybrid solution containing 0.04 mol TEOS.

Melting peak for all three samples is at 179°C. There is no effect of coating on the melting peak of the material. Similarly, crystallization peak of all three samples is at around 120°C. There is no effect of coating on crystallization peak of the material.

CHAPTER-6

APPLICATION

6.1 Packaging of bread in pouches made of coated BOPP:

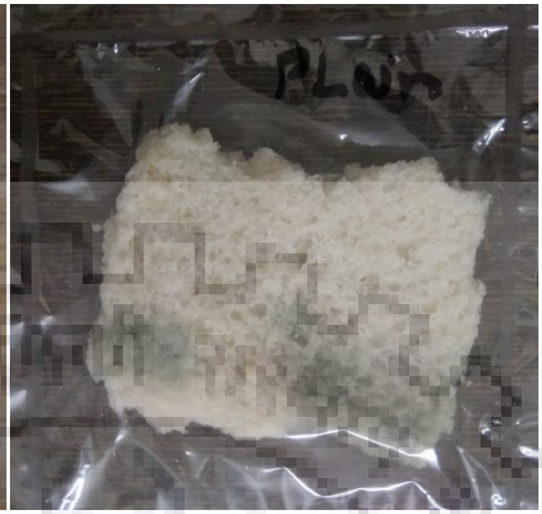
5 different pouches are formed. Bread is packed in these three side seal pouches.

Table-2

pouch	Material used
Pouch-1	Plain BOPP without coating
Pouch-2	Plain BOPP coated with hybrid sol containing 0.02 mol TEOS
Pouch-3	Plain BOPP coated with hybrid solution containing 0.04 mol TEOS (cylinder coating)
Pouch-4	Plain BOPP coated with hybrid solution containing 0.04 mol TEOS (dispersion coating)
Pouch-5	Plain BOPP coated with hybrid solution containing 0.05 mol TEOS (dispersion coating)

These pouches are placed in room condition after packaging of bread to check the shelf life of bread. There will be difference in shelf life of different sample because of difference in oxygen transmission rate. Now the following pictures show the change in bread pieces packed in different pouches after 9 days:

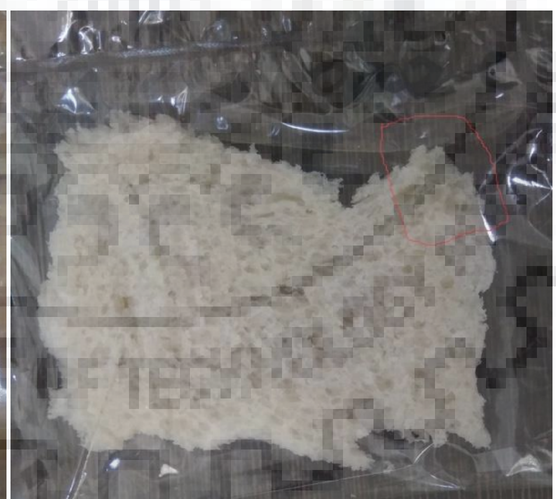
Pouch-1



9 April, 2019 18 April, 2019

We can easily see the growth of mould over the period of time. Growth is due to transmission of oxygen through pouch.

Pouch-2:



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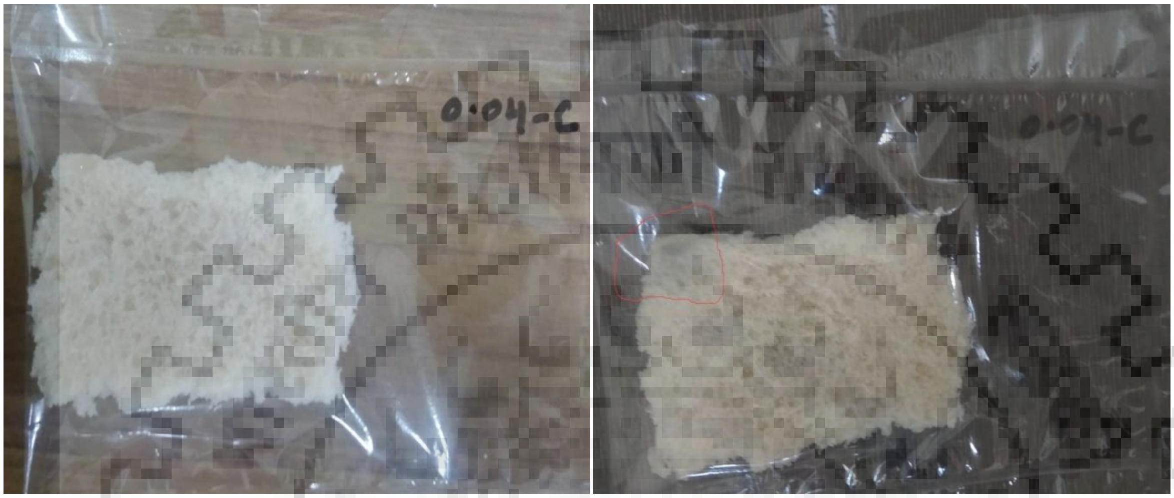
This pouch is made of BOPP cylinder coated with hybrid solution containing 0.02 mol TEOS. So due to reduction in oxygen transmission mould growth is very less as compared to without coating BOPP pouch. Growth of mould is shown in red circled area.

Pouch-3:



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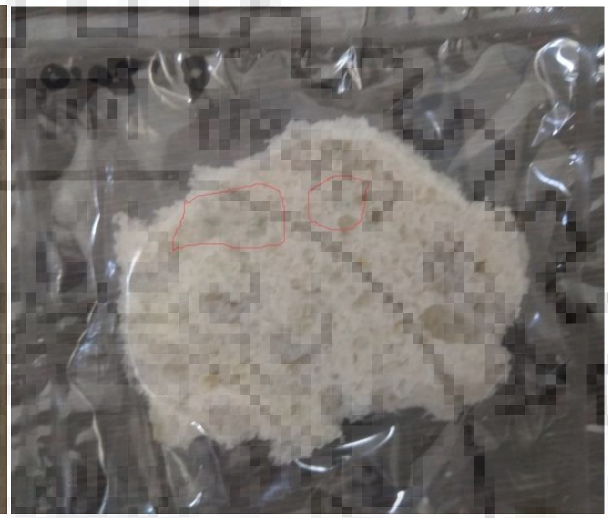
This pouch is cylinder coated with hybrid solution containing 0.04 mol TEOS. In this sample also shows very less mould growth due to reduction in OTR value.

Pouch-4:

9 April, 2019 18 April, 2019

This pouch is also made of BOPP coated with hybrid solution containing 0.04 mol TEOS. But in this sample hybrid solution is coated with dispersion coating. OTR value measured with dispersion coated film is less than the OTR value measured with cylinder coated film. So in this sample there is no mould growth over the period of time.

Pouch-5:



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This pouch made of BOPP dispersion coated with hybrid solution containing 0.05 molTEOS. In this sample there is just beginning of growth of mould as it is shown in red circle area. OTR value of this sample is lesser than all other samples except BOPP dispersion coated with hybrid solution containing 0.04 mol TEOS.

CONCLUSION:

In this study hybrid solution is prepared to coat on BOPP film. Components in hybrid solution are selected such that there is superior phase compatibility in solution. This solution is cylinder coated and dispersion coated on BOPP film and oxygen transmission rate reduces to 92 and 72 cc/m^2.day respectively as compared to oxygen transmission rate of plain BOPP film (1500-2000 cc/m^2.day). Reduction in OTR value is due to presence of inorganic component and its phase compatibility with organic phase because of the hydrogen bonding. Haze value (%) of coated film also increases due to reduction in crystalline behaviour. While using hybrid solution with TEOS content of 0.04 mol, results are much better. If we increased this content, OTR value is increased as compared to BOPP coated with solution having TEOS content 0.04 mol. This can be due to the cluster formation of inorganic material in hybrid solution and because of that micro phase separation occurs.

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