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Experimental analysis of property variation in biaxially oriented polypropylene film (CBSX30 EH) during storage

Ajitanshu Vedrtnam[1], S.J.Pawar[2]*, Ramesh Pandey[2]
Department of Applied Mechanics,
[1]Research scholor, MNNIT, (ALLAHABAD)
[2]Associate Professor, MNNIT, (ALLAHABAD)
E-mail: sjpawar@mnnit.ac.in

ABSTRACT

It has been observed as potential problem by many of the polymer manufactures that the polymer films like Biaxially Oriented Polypropylene (BOPP) experience degradation in their properties during storage. Usually, if not complete stock of films, than at least 10-20% of the complete stock experiences properties degradation. The present study is conducted for finding out the extant of variation of film properties like frictional coefficient, haze, gloss, and tensile strength. BOPP film is analyzed after subjecting it to aging and aging in sunlight/artificial light that cause accelerated aging. It was concluded that the storage condition affect the properties of BOPP Film. The film experiences maximum degradation if subjected to artificial light and least degradation when kept in dark. The remedies against degradation are also suggested.

KEYWORDS

BOPP;
Frictional coefficient;
Gloss;
Haze;
Tensile strength.

INTRODUCTION

A CBSX30 EH thermal film is Biaxially Oriented Poly Propylene (BOPP) film, introduced about 30 years ago as a supplement to cellophane film, but now it is the most preferred material for functional flexible packaging. BOPP film is produced by stretching Polypropylene in both the machine direction (MD) and cross direction (CD). BOPP has become major material for flexible packaging because of its superior strength at low gauges, uniformity, clearness and good printability. The film can be manufactured as heat sealable or as non-heat sealable material and in either case produced as white opaque, pearl luster or clear transparent film. Certain additives (Epoxy and Polyurethane Resin) and Accelerators (Styrene Gel, Methyl Ethyl Ketone Peroxide, Silane and Cobalt Naphthenate) are usually added to improve its properties related to slip. They also modify the heat seal temperature and anti static requirement.

Optical properties of Polyolefin film (Polyethylene (PE), Polypropylene (PP), Poly Methyl Pentene (PMP), and Polybutene-1 (PB-1)) like transparency, haze etc. are significant for applications resembling the packaging applications in industries. The loss of transparency (Haze) is mainly owed to the light scattering from the interior of the film as well as from the film surface. Often spherulitic morphologies (sphere like semi-crystalline regions in an un-branched linear polymer) are one of the sources of bulk scattering in semi-crystalline polymers. The interior or bulk scattering is also originated by fluctuations in refractive index of polymers which occur on the length scale of the wavelength of visible light (400–700 nm). Normally, surface roughness, surface defects and micro-structural variations at the surface causes light scattering at an air-film interface. It is now generally recognized for oriented Polyolefin films that the loss of transparency is primarily caused by surface scattering rather than by interior scattering.

In accordance with the surface roughness of Polyolefin films, and hence transparency of polymer films depends on the molecular weight of polymer, presence of nucleation agents, polymer melt elasticity, frost line height, speed of extrusion and cooling during film manufacturing as established in[1] [2]. In order to reduce the crystalline haze one can lower the crystal size which can be achieved by adding suitable nucleation agents. In addition, crystalline haze can also be lowered by lowering the frost line height.

Gotzen et al[1] have investigated thermal properties and effect of aging in three layered BOPP film, they also compared the differences in measurement with a Wollaston wire probe versus the nano scale probe in nano-TA. Nano-TA was found more sensitive in measuring onset temperature and showed more distinct differences in transition temperature for fresh and annealed BOPP film compared to micro-TA. Galic et al[2] have conducted study on high speed overwrapping film with shrink tightening properties, co-extruded on both sides with heat sealable Polyolefin copolymers. They have got excellent sparkling appearance, balanced shrinkage, enhanced machine performance, excellent moisture and flavor barrier, differential slip properties for tight wraps, and resistant to solvent attack. They also found that in high speed wrapping, slip should be low profile and film should be kept below 30 °C before being employed. Oliveira et al[3] have studied surface configuration and adhesive properties of BOPP film with the help of corona discharge. Chemically active sites on surface of BOPP film are formed by corona discharge. The active genus formed in air was used to form graft copolymerization of Acrylic Amide. The extent of grafting or electron spectroscopy characterized the surface formation, hydrophilicity and adhesion of the grafted BOPP film. Ho et al[4] have studied the effect of alteration of antioxidant by ultra violate (UV) treatment on dielectric strength of BOPP capacitor film. Improvement in breakdown strength was observed and it was also found that an electric field can cause dissociation and ionization of molecules, which results in formation of free molecules. Arvanitoyannis et al[5] have conducted an experiment in which PP was photo oxidized under polychromatic light ($\lambda \geq 300$ nm) at different intensities of the incident light. The variations of intensity were obtained without changing the relative spectral distribution of the source or the temperature at the surface of the exposed samples. Philippart et al[6] exposed PP samples to artificially accelerated photo ageing in various conditions of light intensity. The aged samples were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) techniques coupled with chemical derivatization to determine the degradation structures resulting from UV exposure. Chemical titrations of the Hydro Peroxides and determinations of the oxygen consumption were carried out to quantify the formation of the oxidation photoproducts. Results showed that modifying the exposure parameters induced notable changes in the reaction kinetics. These changes also led to some modifications of the relative concentrations of the various oxidation photoproducts, particularly those of the carbonylated products including Esters and Carboxylic acids. Yang et al[7] exposed photo chemically unstabilised PP films in reactors equipped with a fluorescent lamp at different temperatures and proposed a way for developing a lifetime model for the photo oxidation of PP films. Jarus et al[8] studied the evidence from chemiluminescence analysis by the heterogeneous model. The film was re-examined and it was concluded that heterogeneous model yielded better result than homogeneous kinetic model. Kata et al[9] studied surface morphology of thin films of Isotactic Polypropylene (iPP) and compared the thermal and mechanical properties of iPP films irradiated by gamma ray in an acetylene atmosphere after uniaxial expansion. The changes in morphology, crystallinity and tensile parameters (yield stress, rupture stress and elongation strain) of the PP with irradiation were investigated. The results showed some evidences of gel formation due to cross linking and/or long chain branching induced by radiation. Chu et al[10] studied the changes occurring in the super molecular structure of PP film when pigments were introduced. It has been established that pigments cause changes in the dimensions within the volume of the crystallites as well as in density and optical birefringence. The internal orientation, characterized by the value of infrared dichroism, is also essentially changed. Lekaye et al[11] proposed a method for the measurement of the degree of orientation of crystalline segments in PP films using results of IR polarization spectra. Xiaoqing et al[12] found that the pressure expansion can be used to improve the piezoelectric d_{33}-coefficients of customary cellular PP films. Chen et al[13] found grafting reactivity of electron beam pre irradiated PP film by grafting of Acrylic Acid (AAc) and Acrylamide (AAm) repeatedly or intermittently. An interpenetrating polymer networks (IPN) with both temperature and pH sensitive properties were obtained by two times grafting of AAm and AAc onto preirradiated PP film. Benkhenafou et al[14] studied an aging of polymers resulted from structural modifications at the molecular level and influence of structural factors on the fracture properties of PP. Balas et al[15] studied the influence of annealing temperature on the fracture properties of iPP films. The fracture behavior is studied by means of the Essential Work of Fracture (EWF) procedure, and was complemented by the study of the effect of thermal treatment on tensile properties and microstructure, using differential scanning calorimeter (DSC) and wide-angle X-ray scattering (WAXS). It was shown that the initial meta-stable phase of quenched iPP films transforms gradually into the monoclinic form as the annealing temperature is increased, resulting in an important improvement of the tensile properties, whereas the fracture parameters have different evolutions depending on the Ethylene content. Mrkic et al[16] studied the permeance of carbon dioxide, oxygen, nitrogen, and air through commercial polymers based on PE, BOPP, and PA used for food packaging. The influence of temperature (from 10 to 60 °C) and crease stress cycles (30, 50, 70, and 110) on gas permeance was also analyzed. The highest variation in gas permeance changes with increased stress cycles were observed with films having a metalized layer in the structure, namely BOPP coex. Lin et al[17] studied the effect of thermal history on the transparency of BOPP films. The clearest films were obtained from compression molded sheets with the most homogeneous texture and by orienting it at the lowest temperature. As discussed by Mathlouthi[22] for blown Polyethylene films, there are two fundamentally different sources of surface roughness. First, a very low melt elasticity and second a very high melt elasticity. The former assists in the formation of spherulitic-like superstructures in polymer films at or near the surface. However, later causes a fine-scale surface roughness owing to instabilities in an elastic melt. It was also reported that the choice of a proper resin with a proper melt elasticity and molecular weight can minimize the surface haze.

BOPP thermal films lose their properties under storage. The probable reasons are effect of high temperature, UV exposure, aging, and shrink tightening due to high speed of manufacturing, surface structure, adhesive properties, permeability due to exposure to specific gases, moisture, handling, self weight, and friction coefficient. Polymer loses their properties as free radicals are formed in polymer which further accelerates degradation when exposed to UV radiation.

EXPERIMENTATION

The experiments are conducted by simulating the storage conditions with the actual storage conditions in the firms and following the standard ASTM Procedures[18-21]. The samples are taken from Jumbo coil in the required dimension as mentioned in the standard for associated test. Every reading is an average value obtained after testing three samples. The films are examined for six months at different intervals and variations in properties are recorded/ obtained. Coefficient of friction (Cof), haze, gloss, and tensile strength are considered for study in this work as they are most crucial properties in the applications like packaging and lamination. Testing is done based on the specific duration causing significant change in property (variation more than 0.2 % of property value) associated during that period. The tensile strength & elongation of film are tested as per ASTM D-882. Samples of 25x25 mm^2 are prepared by cutting the test specimen from the Jumbo coil in such a way that the test specimen from all the three sides (left, centre, and right) are obtained, both in machine direction and transverse direction. Three specimens from each side and both direction are tested. The average values are calculated and reported here. Cof was tested at a regular interval, after one day interval for first 15 days and then after two days interval for the remaining period, using ASTM D1894-14. Samples are taken by the similar procedure as in tensile testing. During the test, samples are held on the test bed by means of the vacuum channel and magnet strip so that the film surface remains flat, smooth, and unstretched. Then the sled is drawn by drive mechanism at constant speed required by the test standard in use i.e. (150 mm/min.). The static and dynamic friction coefficient are calculated using equation 1 and subsequently displayed digitally,

$$\mathbf{Cof = A/W} \qquad (1)$$

Where A = force in gram and W = sled weight (200 gms).

Haze is measured following ASTM D1003. For every single reading, three specimens free from wrinkle, ripple, dust or any type of physical defects each from left, center and right of around 100 x 100 mm^2 area were taken. Gloss was tested following ASTM D2457 using gloss meter of 45° angle geometry. Specimens are prepared following same procedure as for measurement of haze. The effect of UV rays is measured using artificially designed set up[6] and also by exposure of film to sunlight (Temp. 32 °C and 55 % humidity (Average Value)).

RESULT AND DISCUSSION

The results are given for film subjected to normal storage condition in TABLES 1-3, however, TABLE 4 shows results for film subjected to controlled storage conditions (sunlight, artificial light, and dark). TABLE 1 shows the variations of Cof, both for film to film and film to metal. It shows irregular variation of Cof, however a downtrend is observed over the test period. It is also observed that film to metal Cof is lower than film to film Cof and significantly large downtrend in Cof of film to film is observed than Cof of film to metal. The higher values of Cof that are observed intermittently which causes irregular variation may be due to variation in the samples that are taken from Jumbo coil which was aged for stated period. Such variation of Cof is

TABLE 1 : Time dependent variation of coefficient of friction (Cof)

Day (no.)	Cof (film to metal)	Cof (film to film)
1	0.24	0.42
3	0.23	0.30
5	0.20	0.28
7	0.22	0.31
9	0.22	0.27
11	0.21	0.26
13	0.20	0.28
15	0.22	0.27
18	0.21	0.26
21	0.20	0.26
24	0.20	0.24
27	0.19	0.25
30	0.19	0.22

TABLE 2 : Time dependent variation of haze and gloss

S. No.	Day (no)	Haze	Gloss (%)
	1	1.3	90
	4	1.2	91
	8	1.1	90
	11	1.6	92
	15	1.2	92
	19	1.2	90
	23	1.1	91
	27	1.1	90
	30	1.1	90

TABLE 3 : Time dependent variation of tensile strength and elongation

Day (no.)	Tensile strength (kg/cm^2)		Elongation (%)	
	MD	TD	MD	TD
1	157	230	240	64
4	144	228	236	64
8	148	230	236	59
11	147	206	218	56
15	131	212	180	44
19	140	210	187	49
23	138	216	185	48
27	140	215	180	47
30	135	208	181	47

caused due to aging and available storage conditions. It is also pertinent to note that Cof of film to film shows greater downtrend owing to the aging of both films. Lesser Cof is undesirable for applications like lamination.

TABLE 2 shows the variation of haze and gloss for 30 days. It shows that the value of haze become almost constant after twenty days from the polymer film manufacturing. It is also found that lesser value of haze than the initial value of haze is settled after initial settlement period. The highest value of haze that is observed intermittently (at 11th day) may be due to variation in the samples that are taken from Jumbo coil that was aged for stated period. However similar intermediate variations are also observed in Cof as well. Such variation of haze is caused due to aging and available storage conditions. Lesser value of haze is undesirable for most of the application of BOPP like lamination and packaging. The steady value obtained after thirty days is acceptable for most of the applications except in high valued packaging applications. The value of Gloss does not change as much over the test period however similar to Cof and haze it also shows a higher value at intermittent time. Dust, dirt, and pollution free storage is required for maintaining gloss to acceptable value. The intermittent rise in the Cof, haze, and gloss may need further detailed and long term investigations to be supported by polymer degradation kinetics.

The variation of tensile strength and elongation is presented in TABLE 3. It shows that the tensile strength decreases in both MD and TD. The percentage elongation before fracture also decreases. Such variation of tensile strength is caused due to aging and available storage conditions. It is important to note that the tensile load on polymers produces initial deformation as a result of alignment of molecules (Bond-strengthening and bond-lengthening). However, a permanent deformation in polymer occurs as a result of slip between adjacent molecules due to weaker attractive forces between them. Lesser

TABLE 4 : Effect of UV exposure on properties after 15 days

Property	BOPP Film (New)	Dark	Artificial source	Sun-light
CoF (film to metal)	0.24	0.22	0.18	0.20
CoF (film to film)	0.40	0.32	0.28	0.29
Gloss	1.2	1.2	1.2	1.1
Haze	90	88	83	86
Tensile strength (TD)	110	102	89	98
Tensile strength (MD)	220	207	192	200
Percent elongation (TD)	200	190	182	194
Percent reduction (MD)	50	48	44	47

TABLE 5 : Effect of UV exposure on properties after 35 days

Property	Dark	Artificial source	Sunlight
CoF (film to metal)	0.20	0.16	0.18
CoF (film to film)	0.24	0.20	0.22
Gloss	1.1	1.0	1.1
Haze	87	80	86
Tensile strength (TD)	101	94	97
Tensile strength (MD)	205	185	195
Percent elongation (TD)	189	174	192
Percent reduction (MD)	50	39	46

value of strength is undesirable for the application like lamination and packaging.

TABLES 4 and 5 shows the collective effect of UV rays and aging on the selected properties. The effect is measured after subjecting the film to direct sunlight, artificial light[6], and also when film is kept in dark

The results are reported for 0th, 15th and 35th day as the preliminary tests indicate that above period shows significant variation in most of the properties. Considering Cof values on 0th day as a benchmark, result specifies that the film kept in dark for 15 days have about 9.3% less Cof (film to metal) and 20.2% less Cof (film to film). On the other hand, after 35 days, it has around 17.1% lesser Cof (film to metal) and 39.8% lesser Cof (film to film). It clearly indicates that Cof strongly depends on the number of storage days. It is worth mentioning that Cof on 0th and 15th day have almost same values as that were obtained when the film was kept in normal storage and the Cof degrade most when subjected to artificial light and aging collectively. Value of gloss remains same as the initial value on 15th day when film is kept in dark however it deceases by 8.9% when kept in artificial light. Gloss decreases by 8.9% on 35th day when kept in dark and 16.7% when exposed to artificial light. However it follows the general trend as it has maximum value when less aged and stored in dark or in normal storage condition then it is having a lesser value when subjected to sunlight and it is least (16.7% less) on 35th day and when subjected to artificial light. Reduction in Gloss by 16.7% as compared to the initial value is acceptable for most of the applications. Haze degrades by 2.8% on 15th day when kept in dark, 4.5% when subjected to sunlight and 8.8% if subjected to artificial source of light. The result reported indicates 4.1%, 4.8%, and 12% reduction in haze is observed when kept in dark, subjected to sunlight and artificial light sequentially on 35th day. Tensile strength decreases by 8% in TD, 6% in MD direction on 15th day when film is kept in dark, 19% (TD), 13% (MD) when subjected to artificial light. However, when subjected to sunlight, it has intermediate value. Whereas on 35th day tensile strength decreases by 6.9% in MD and 8.9% in TD, when kept in dark. It decreases around 11.5% (MD) and 11.9% (TD) when subjected to sunlight. A further reduction in tensile strength was noted when film was exposed to source of artificial light. It decreases by 15.9% (MD) and 14.5% (TD). Overall the film stored in dark shows the better properties then film exposed to sunlight and artificial light.

Film properties have intermediate value when subjected to sunlight as compared to dark and artificial light. It is also worth mentioning that properties when it was kept in dark were quite close to the values in normal storage condition (closed room) except in few cases as the storage may be having little exposure to sunlight. The reason for same is quite obvious that artificial light sources emit higher UV intensity than sunlight, however the dark storage have least UV exposure. Accelerated aging is caused due to formation of free radicals in the BOPP films that further causes quick degradation in films.

CONCLUSION

The data obtained from experiments has proved to some extent that aging, UV rays exposure, and temperature variation plays important role in deviation of properties of the film. During experiments, it has been observed that the Cof ((film to film) and (film to metal)) reduces over the period of time, except an odd marginally higher intermediate value (less then initial value) of Cof (film to film) on 9th day. Haze also shows the down trend but not as significant as in Cof. Gloss does not change much when film is kept in normal storage condition. However, both haze and gloss decreases when film is subjected to high intensity UV radiation. Gloss shows 16.7% reduction and haze reduces by 12% on 35th day when subjected to artificial source of UV radiation. Tensile strength decreases as the film gets aged, it significantly reduces if film is subjected to aging and sun-light collectively, it reduces by 15.9% (MD) and 14.5% (TD) when subjected to artificial light on 35th day. BOPP film is affected when subjected to artificial UV radiations and all the selected properties experience reduction. Similarly when film is subjected to sun-light it shows marginal reduction in properties and when kept in dark it shows very less reduction in properties. So it can be concluded that storage condition affect the properties of BOPP Film. Thus, any light source giving yellow light can have detrimental effect on the film, hence the use of bulb should be avoided and CFL may be used in the storage room, additionally it is recommended that the safe storage time may be limited to 15 days at the storage.

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