Cellulose And Cellulosic Film In Packaging

P. S. Hariharakrishnan

The supermarket culture of individually packed consumer goods such as food and pharmaceuticals where the packaging is discarded immediately brings with it the problem of instant waste. Consideration of the disposability or potential for salvage and re–use of the packing material is now drawing the increasing attention of package designers and packing material manufacturers.

New materials, such as plastics, that are of a persistant nature and are not disposed of easily and naturally are already creating problems for disposal. Such a problem does not exist with Cellulose film and thus has an edge over other films (plastic films). A thin cellulose film wrap with its even thinner fnnctional coating is the simplest and the lightest packaging material that can be used to protect perishable foods and pharmaceuticals.

By special coating and or lamination, Cellulose film can achieve a degree of protection for majority of packaging requirement. When the content of a cellulose film package is taken out the low bulk and light weight of the pack make it easy for the consumer to pocket and bin the litter and later dispose it off.

P. S. Hariharakrishnan
Chief Chemist
The Travancore Rayons Ltd.
Kerala

In the ecology, Cellulose film comes from nature and returns to it easily. Cellulose film can be incinerated very easily. It burns off forming Carbon dioxide which is used by plants. Land fill also returns the constituents of Cellulose film to the natural cycle by another route. The thin coating and printing inks fall off and disintegrate into compost.

From the fore-going it is clear that cellulose and cellulosic films is going to play an important role in the functional packaging of consumer goods of foods and pharmaceuticals.

Cellulosic films that are commercially made are :

1) Cellulose Acetate
2) Hydroxy Ethyl Cellulose
3) Cupraphane–Regenerated cellulose by the Cuprammonium process.
4) Cellulose fiim–Regenerated cellulose by Viscose process.

We shall now deal one by one the above films and assess its status and potential.

1) Cellulose Acetate Film

Cellulose acetate is the cellulose plastic most widely used in film manufacture. High viscosity and high acetyl content cellulose acetate are used in the manufacture of film with 10–15% of phthalate plasticizer. It is made by casting from solvent solution and by extruding the thermoplastic in suitably designed equipments.

The film is transparent, odourless, tasteless & non-toxic. It is insensitive to softening by water but has high rate of water vapour and gas transmission. The dimensional stability is good. By its inherent properties, particularly high gas and water vapour transmission it has little protective value for food and pharmaceuticals. However, it finds applications as a transparent see through window in bags, boxes and cartons. Since the field of application is limited, cellulose acetate film as a packaging material has not shown much impact and the growth is very limited.

2) Hydroxy Ethyl Cellulose Film

The alkali soluble hydroxy ethyl cellulose, i. e. the one having a lower degree of substitution of hydroxyl groups of cellulose is used for the preparation of film. It is made by the reaction of alkali cellulose with ethylene oxide at controlled condition for obtaining the required degree of substitution, dissolving the hydroxy ethyl cellulose in dilute alkali, purifying the solution so obtained and regenerating the hydroxy ethyl cellulose by extrusion into dilute acid followed by washing and drying. Rayonier had obtained a number of patents on the preparation of hydroxy ethyl cellulose and manufacture of film from there off.

The film obtained had similar properties to regenerated cellulose by the viscose process, which will be dealt in detail later but has not become a commercial success since the film shrinks considerably on heating and a substantial portion of cellulose film are used with heat seal. Due to this deficiency, though some units started manufacture of hydroxy ethyl cellulose film, they had either stopped the manufacture or are producing some special types such as twist wrap. Thus this film could not become a commercial success even though from theoretical consideration it had a lot of potentiality.

3) Regenerated Cellulose film by the Cuprammonium process

In this process film is regenerated from a solution of high alpha cellulose (cotton linter pulp) in cuprammonium by extruding into settling and regenerating bath containing sodium hydroxide and sulphuric acid respectively. The film obtained will then be washed free of chemicals, and softened by aqueous solution of glycerol or other humectants and then dried. The plain film obtained can be coated to give added properties.

The only **advantage** in this process for preparation of regenerated cellulose film (from the viscose process that is described later) is that film of 15 to 25 gms. per m^2 can be made by this process. The properties of the film is akin to that obtained by viscose process. The cost of production is very high due to the cost of copper salt and the recovery cost of the same. The film hence is very costly compared to film made by the viscose process, and hence this process has not established itself on firm ground commercially.

4) Cellulose Film

Regenerated cellulose film by the viscose process is the most important and largely produced cellulose film today. The percapita consumption of different types of cellulose film is about 16 lbs. in the USA and 9 lbs. in West Germany. Compared to this the installed capacity of Cellulose film in India is 25 tonnes per day which approximately works out less than 0.5 lbs. per head, Thus there is considerable scope for expansion of cellulose film in India in the years to come even though there is a market slump for it at present. With the severe competition in packaging from the different plastic films, cellulose film had stood well and continues to grow. The dominant role cellulose film has played in packaging over the years has been the result of how it had met the problems that confront the modern packager–protection of product, product needs, cost, merchandising, convenience, production and needed shelf life to give the product the best sales position in the market. This is mainly due to the variety of properties which cellulose film can be given.

It would be appropriate to deal with the various aspects of cellulose film to understand and appreciate this versatile packaging film.

The history of regenerated cellulose may be considered to start with the discovery by Cross, Bevan and Beadle in 1892 that cellulose could be converted into a soluble form by treatment with caustic soda followed by carbon bisulphide. This reaction is known as xanthation and the solution that could be made from the product of xanthation is known as viscose. A method for the coagulation and regeneration of cellulose in the form of foil was patented by Stearn in 1898.

Branden Berger, the Swiss Chemist and Engineer was largely responsible for the initial work on the production of regenerated cellulose foil in continuous sheets and his first patents for continuous casting machine were issued in 1911. Brandenberger is also credited with the coining of the familiar trade name "CELLOPHANE" which is derived from the first syllable of cellulose and the last syllable of the French word diaphane (transparent). Today 'Cellophane' has become a common name and regenerated cellulose film is commonly referred to as Cellophone throughout the world. However, a few of the well known manufacturers continue to use it as trade name.

The first plant for the production of cellulose foil was started in France by La Cellophane. Shortly after the first World war production commenced in Great Britian and USA using substantially the Brandenberger process under licence from La Cellophane.

The product produced in the early stages was costly and had somewhat restricted application owing to its high transmission of water vapour. The development of methods of moistureproofing cellulose film around 1930 increased the potential applications and the demand for cellulose film increased. With increase in production, the price of the material fell sharply. Today, regenerated cellulose film must compete with film based on polyethylene, polypropylene and other plastics. Until the prices of these become considerably lower than cellulose film and their printing and machinability considerably improved, regenerated cellulose film will continue its preference in its main fields.

The manufacture of regenerated cellulose film in India commenced in December 1949 as a result of the pioneering effort of late Shri M. Ct. m. Chidambaram Chettiar, founder Chairman of Travancore Rayons Ltd. The plant that went into production at the time had a production of one ton per day only. Travancore Rayons Ltd. had since increased their production by 15 fold. In mid 50s Kesoram Rayons Ltd. put up a plant for manufacture cf cellulose film in West Bengal. Both the units has since expanded their production and are now equipped to produce 25 tons per day.

Cellulose film is regenerated cellulose in the form of transparent clear continuous film The starting raw material in the manufacture of cellulose film is chemically pure cellulose. The manufacture of cellulose film requires vast facilities and complex technology. The first step in the manufacture of regenerated cellulose film is the production of alkali cellulose. Chemically pure cellulose is steeped in 17–20% sodium hydroxide solution at controlled temperature and time determined by the precise characteristic of the pulp. During this treatment, cellulose swells and some of the hemi cellulose are dissolved. The alkali eellulose so formed is then pressed to remove excess alkali. The pressed alkali cellulose is then shredded in specially designed equipment at controlled temperature to a crumb density of 150–200 gms. per litre.

The alkali cellulose obtained contains 15-16% sodium hydroxide 30–36% cellulose and rest water. The steeping solution which is pressed out contains the hemicellulose which are dialized to remove it and the soda returned to the system for use again.

The shredded alkali cellulcse is allowed to age at controlled temperature and humidity. At this stage oxygen is absorbed and the length of the cellulose chain is shortened. This step is necessary to obtain viscose of desired viscosity at subsequent processing. The ageing takes about 12 to 30 hrs. depending on the requirement of the process and the molecular weight of the pulp used and temperature of ageing.

Ager ageing, alkali cellulose is charged into churns which are cylindrical vessels rotating on horizontal axis.

After charging the alkali cellulose, the churns are closed, rotated slowly, evaculated pre-determined quantity of carbon bi-sulphide is admitted. The reaction namely that of the alkali cellulose and carbon bi sulphide is exothermic and the churns have provision for cooling. The reaction takes place initially at a temperature of about 20 deg. C. which is permitted to rise to about 30 deg. C towards the end of the cycle. A typical cycle requires about 150 mts. After completion of the xanthation reaction the excess of carbon bi suiphide is vented and sodium cellulose xanthate which is bright orange yellow in colour owing to the presence of sodium trithio carbonate is dumped into turbine mixers where it is dispersed or dissolved by stirring in dilute caustic soda solution. A temperature of about 10-20 deg. is maintained during the process, and required about 3 to 4 hours. The solution so obtained contains 7 to 8% cellulose and 5 to 6%

caustic soda and is commonly referred to as viscose.

The chemical reactions involved in the preparation of viscose may be represented by the equations :

$$ROH+NaOH=RONa+H_2O.$$

$$RONa+CS_2=RO\text{-}CS\text{-}SNa.$$

Where R represents the cellulose molecule.

Viscose obtained contains undissolved cellulosic impurities and air. The particles are removed by filtration through cloth in plate and frame filter presses. The filtered viscose is ripened by storing in ripening tanks for a period of 30 to 40 hours at controlled temperature. The air contained in viscose is removed by applying vacuum to the ripening tanks. The ripening is followed by observing the viscosity and salt index or Hotten Roth as the ripening should not be allowed to proceed beyond a certain level.

When the viscose has ripened to the desired degree it is pumped to the casting machine of the film forming plant. The thickness of the film can be controlled by regulating the opening of the lips in the hopper through which the viscose is injected in a thin stream and by controlling the rate of flow.

The viscose falls from the casting hopper into coagulating bath which coniains 10-15% of sulphuric acid and 14-20% of sodium sulphate and is maintained at a temperature of 35-45 deg. C. In this bath the viscose is first coagulated and regenerated back into cellulose.

Most forming machines consists of a series of tanks containing rollers and guides which guides the film through a sequence of treatments. The treatments that follow one after another in the machine are :

Completion of regeneration in dilute H_2So_4.

Hot water washes for the removal of gases and sulphur.

Bleaching.

Antichlor and.

Finally softening and finishing.

Between each treatment, there will be water washes. The film after passing through the finish bath enters the drier through a set of squeeze rolls. The film after drying is wound on rollers.

The film is produced at a speed of 50 to 100 meters per minute and the width of the fillm will be about 50 to 54".

The Casting operation described above gives plain transparent regenerated cellulose film. This is not moisture proof, i.e., allows water vapour to pass through it. Hence it is not suitable for packing of articles which are susceptible to moisture changes. It has its own field of application where moisture protection is not required, like packing of textiles for eg.

When special properties, such as moisture proofness, or heat sealability are required, the film is given a subsequent coating treatment depending on the particular properties required. A typical moisture proof coating consists of Nitrocellulose, Plasticizers, Resins, Waxes dissolved in a solvent mixture composed of Esters and Toluene. The uncoated fiml is passed through the coating bath and dried in a current of hot air and the released solvents are recovered. The fillm during drying loses its moisture also and hence rehumidified to restore its flexibility. The re-humidification is done by passing the film through a chamber maintained at a relative humidity and temperature above the melting point of the hydrophobic agent used. The weight of the coating applied to film varies from 8 to 20% of the weight of the uncoated film.

In recent years cellophane has been challenged increasingly in some major applications by various plastic film. As a result Cellulose film had to share some of its markets. But on the whole it has maintained and even increased its importance as a packaging material. This has been accomplished through a continuous upgrading of types and introduction of new types to give improved or new performance.

These distinct performances result from the nature of Cellulose film itself; a strong, relatively stable substrate supporting a coating material appropriate to the packing need. The most common coating applied is based on Nitrocellulose. The other general categorics of coatings had been developed during the last decade are copolymers of polyvinylidene chloride (Saran type) vinyl copolymer and polyethylene. These coatings are formulated with a number of materials to obtain the specific properties needed for particular end uses of the finished film.

There are more than 120 types of Cellulose film available today. They have the common cellulose film substrate and general appearance. But each type has some special properties which had been incorporated to meet a specific packaging requirement.

Cellulose film producers generally identify the various common types film by letter designation Some of the common symbols used along with what they indicate are listed below :

A —Anchored
C —Coloured
D —Demi (one side) coated
H —Resistant to blocking in humid atmosphere
J —Flame resistant
L —Less moisture proof than standard
M —Moistureproof
O —Opaque
P —Plain
R —Rancidity retardant
S —Heat sealing
T —Transparent
U —Unsized, low surface-slippage
XX—Polymer coated

Thus, the designation MSAT means that the sheet is transparent and has a water vapour resistant coating which is heat sealing and can be used in contact with water.

Since the various characteristic of each type of film are different and in some cases are developed with the particular end use in view, the detailed specification of each type is best obtained from the manufacturer. An idea of the general characteristic of the most common types are useful and are given below :

1) Substance :

The Cellulose film of different thicknesses are made. These are generally referred to as gauges. Numerically gauge represents the weight in gms. of 10 m^3 of film. The common gauges in which the film is manufactured are 300, 400 and 600. The substance (weight per square meter) of the different gauges are as shown.

	Wt. gms/m^2
Gauge 300 Plain	29–34
Gauge 300 Coated	32–37
Gauge 400 Plain	38–45
Gauge 400 Coated	40–47
Gauge 600 Plain	56–64
Gauge 600 Coated	60–80

2) Moisture Content :

Plain film :	: 9 to 10%
Coated film	: 8 to 8%

3) Tensile Strength :

By this is meant the force parallel to the plane of the specimen required to produce failure in a specimen of specified width and length under specified conditions of loading. The strength of cellulose film is more in machine direction (length) and less in transverse direction.

	300 gauge	400 gauge	600 gauge
Tensile strength gm/mm. Min.			
Machine direction	145	200	300
Min Transverse direction	75	90	110

4) Elongation :

The distance through which the film can be stretched under standard conditions of loading adopted for tensile strength determination till it breaks is referred to as elongation. This is expressed as percentage of the original length In the case of Cellulose film the elongation in machine direction is less and more in transverse direction. The elongation at break of cellulose film generally conforms to all gauges.

Min. % Machine direction .. 10
Min. % traverse direction .. 25

5) Bursting Strength :

Bursting strength is the pressure required to rupture a specimen when it is tested in specified instrument under specified conditions. It is largely determined by the tensile strength and extensibility. Cellulose film of gauges 300, 400 and 600 will have a minimum of 2.25, 2.5 and 3.0 kgm/sq.cm. bursting strength respectively.

6) pH :

The acidity or alkalinity of the film is defined by this characteristic and this is important since certain products are affected by the pH of the wrapper with which it is in contact. The pH of cellulose film will generally be between 5.5 to 8.0.

7) Inorganic content :

The presence of inorganic matter in film will be of interest in selection of the wrapper. The usual specification for packing film covers the chlorides, sulphates and ash content. Various types of film will have slightly different quantities of the above and generally it will be as follows :

Chloride as NaCl % by wt. Max.	0.1
Sulphate as Na_2So_4 % by wt. Max.	0.25
Ash content at 600 deg. C.	0.7

8) Protective quality :

Protective quality of cellulose film is determined by its resistance to the passage of moisture. Depending on the types of cellulose film there will be difference in the protective quality. Since in packing a product the film gets folded and creased, this property of the film is given for film without creasing and with creasing under standard conditions. The normal nitrocellulose lacquer coated film when tested as per British Standard Specification shows the following WVP at 38 deg. C. and 90 + 2% R. H. in 24 hrs. maximum.

Creased	.. 60 gms/m²
Uncreased	... 30 gms/m²

9) Blocking Resistance :

Cellulose film being very smooth shows tendency for surface adhesion and this is reduced by suitable treatment to the required degree. Normally cellulose film will not block when kept under a pressure of 1 kg/cm² at 38 deg. C. and 75% R.H. for 24 hours.

10) Cellulose film has the required flexibility for different uses like high speed wrapping, folding, twisting etc.

11 Heat seal strength :

Cellulose film that are given a coating of heating sealable lacquer can be sealed by heat. The strength of seal is a determining factor in deciding about the weight of content in a heat sealed bag. The heat sealed seam of cellulose film generally has a strength of 100 gms. per inch of seam.

12) Water proofness :

This is a property of coated film. Coated cellulose film is water proof. This characteristic is usually tested by immersing the coated film in water at 20 deg. C. for 7 days or by keeping in boiling water for 10 minutes. Under the above treatment the coating will not blister.

13) Oil proofness :

Cellulose film is impermeable for oil and greases.

14) Maximum use temperature :

The film will char at 190 deg. C. and the coating applied to the film softens from about 100 deg. C. and melts in the range of 115 to 130 deg. C. This behaviour has to be noted in deciding about the maximum temperature of exposure.

15) Minimum use temperature :

All types will not stand freezing conditions. Specially formulated cellulose film is available that keeps its qualities at as low as 0 to 5 deg. C.

16) Dimensional change :

This depends on the temperature and relative humidity of the environment. Normally cellulose film will shrink to the extent of 3 to 5%.

17. Machine Performance :

The machine performance of cellulose film is generally rated as "Excellent".

18) Printability

The film can be printed by normal printing methods and it is rated "Excellent" among flexible materials.

19) Sealing :

Depending on the coating, the different types can be sealed by gum or heat. The heat sealing range of normal types are between 100–130 deg. C The temperature required is depended on the dwell time and preessure.

20) Tear Strength :

The tear strength is low, will easily tear off once torn.

21) Flammability :

Being essentially cellulose it behaves like ordinary paper. But flame proof property can be incorporated by suitable surface coating of film.

22) Gas permeability :

Among flexible films, cellophane has the least permeability for gases.

23) Odour proofness :

Cellulose fim, particularly Saran coated is one of the best odour proof flexible film.

It is observed that cellulose film itself does meet some of the stringent requirements of certain products. These enhanced properties are huilt up by combining cellulose film with suitable other flexible packing materials and this process is known as lamination. A laminate is a product obtained by combining the complete surfaces of two or more webs. The distinction between a laminate and a coating cannot always be drawn.

Most laminates were originally designed to provide increased strength or rigidity. But the widening demands of present day packaging has led to the development of function laminates with properties not possessed by any single material and generally made specifically for a particular application.

Properties of webs are usually combined in the final laminate any may be supplimented by those of the laminating agent.

Cellulose film is used as one or more webs in a laminate and the properties imparted by cellulose film are strength, attractive appearance, low permeability to water vapour, gases, odours and greases and printabilitv.

The following are some of the laminates of Cellulose film that are generally used :–

1. MST–MST Laminate using microcrystalline wax as laminating agent. This has very good protective value.
2. MXXT-MXXT Laminate Lamination effected by heat alone–a good gas. odour, moisture barrier. Low melting is not present in the laminate which can be a hindrance for use in automatic sealing operations.
3. MST–Polyethylene laminate, a medium moistureproof laminate with good flexibility strength, heat seal strength and low temperature performance.
4. MXXT-Polyethylene laminate-This laminate is particularly noted for durability, heat sealability, low permeability to water vapour, good chemical resistance, good low temperature, performance, strength, attractive appearance, low permeability to gases, odours and greases, and excellent printability. There is a good potential for the development of this laminate for the packing of many foods, pharmaceutical and cosmetic items.
5. MXXT–Paper laminate–This combines the properties of saran coated cellulose film and finds use where a stiff laminate is required. Probable area of application such as :

   Soft pack cigarettee packets
   Strip packing
   In outer cover of dry cell
   Pillopacks for biscuits
   Book covers–Paper packs.

A number of other combinations with other flexible films like aluminium foil, coated paper, polymer films other than polyethylene etc. had been developed to meet special requirements.

Extrusion coated and laminated structures using cellophane and polyethylene and polyester films are being employed more extensively each year for packaging a variety of products. These laminates are finding a number of use in vacuum and inert gas packing.

The primary purpose of inert gas and vacuum packing is to remove oxygen from the package and retard mould development, mould and yeast growth and colour fading incurred meats and other undesirable product changes.

The vacuum package is most commonly used with frankfurters, luncheon meats and bacon. The vacuum draws the film down tightly over the product providing intimate film to product contact and excellent appearance. Inert gas packing on the other hand is commonly used for packaging such items as sliced cheese and dried beef to provide a loose pack for easier separation of slices. There are two methods of inert gas packing. In one vacuum gas packing, oxygen is removed by vacuum and replaced with inert gas such as nitrogen, carbon dioxide or a combination of the two.

The second type of gas packing, gas flushing is the method in which gas under pressure is used to flush oxygen from the packing system by feeding gas constantly into the filling tube or into a chamber surrounding the sealing area. It is a simpler method than the first, but uses more gas and may not remove as much of the oxygen.

A few examples of vacuum or inert gas packing gathered from published literatures are given below:

a) **Luncheon meats:**

Oxygen which causes the colour of cured meat to fade when exposed to light must be kept out until the product has been sold. Packaged luncheon meats when stored in the high relative humidity of meat cases, require a film which maintains its oxygen barrier properties when moist. Flat pouches of cellophane and polyethylene had been found useful for this purpose.

b) **Frankfurters:**

The package is stored in high relative humidity and need a film which maintains its oxygen barrier properties when moist. The package must protect the product from deterioration (colour fading) caused by oxygen. One lb. package requires a film of high durability while a half lb. package needs only moderate film durability. Flat pouches of polymer coated cellophane and polyethylene are found useful.

c) **Liquids:**

For small single unit packages of such liquids as soft drinks, syrups, shampoos, frozen soft drinks, flavourings, sauces, and hand lotions, the durability requirements are moderate. A positive seal must be obtained. For most applications laminate of nitro-cellulose coated cellophane and polyethylene can be used. Laminate of saran coated cellulose film and polyethylene–provides a better barrier to essential oils, aromas and flavours.

d) **Sliced cheese, Dried beef :**

Prevention of mould growth is essential. The product is stored in the high relative humidity of refrigerated case and needs a film that retains its oxygen barrier properties when moist. Inert gas packing in laminate of saran coated film with polyethlene will suffice where durability is not critical. Where greater durability is required, laminate of Mylar and polyethylene is preferred.

e) **Nuts:**

The product is subject to rancidity, stales quickly and requires high film durability. The shelf life is variable depending on marketing conditions and requirement should be checked carefully. For best protection gas packing is recommended. For moderate shelf life laminate of polyethylene with N.C. coated cellulose film and for prolonged shelf life laminate with saran coated film are recommended. MXXT-MXXT laminate will function well where gas packing is not used.

f) **Chips and Snacks:**

The product are particularly sensitive to moisture, subject to rancidity and stales quickly. The laminate should provide good durability and high speed performance on make and fill equipments. It must also provide a comparatively stiff bag for better appearance and good display. Most products in this category are packed in MXXT–MXXT laminate, Laminate of Saran, Polycoated cellulose film and cellulose film with coating of saran and Mylar (Polyester).