Modern Food Packaging Technologies: Regulatory Aspects and Global Trends Prof Prem Prakash Srivastav Department of Agricultural and Food Engineering Indian Institute of Technology Kharagpur Week – 05 Lecture – 22

 Welcome to the NPTEL online certification course On modern food packaging technologies regulatory aspects and global trends. In the last lecture we have been seen the different properties of the plastic materials like optical properties, tensile properties, bursting strength, impact strength and tear strength. Now, let us see in the present lecture some more properties of the plastic materials. The next important property is the stiffness.

 If stiffness or flexural rigidity is the opposite of softness or limpness all the properties which find important applications in package use and sales appeal. Stiffness can be considered as the resistance of the film to distortion and in particular to bending. It depends on the thickness of the film as well as the inherent stiffness of the material. Young's modulus is one measure of the inherent stiffness of a single ply film.

 There are also more direct methods of measuring stiffness such as the use of the handleo-meter stiffness tester that measures handle which is the combined effects of flexibility and surface friction of film. The data generated has been shown to correlate well with the actual performance of the material in production processes and finished product performance. The handle-o-meter has a flat plate to hold the sample over a slot. A penetrator beam that pivots on a cam and forces it into the slot and a strain gauge to sense the force reported in grams exerted against the beam by the sample. Stiff materials offer greater resistance to the motion of the beam as it moves into the slot.

 The resistance to repeated flexure or creasing is another important property of the plastic material which is used for the packaging is measured by repeatedly folding the film backward and forward at a given rate. The number of cycles to failure is recorded as the flex resistance. Even if failure does not occur certain properties of the film may be seriously impaired. For example, permeability may be increased or tensile properties may be reduced or optical properties may be seriously affected. For this reason another way of testing crease or flex resistance is to subject the film to a given number of cycles in the test equipment and then compare the relevant properties with those of the uncreased films.

The ASTM F392 method for flex durability is valuable in determining the resistance of

flexible packaging materials to flex formed pinhole failures. It uses Galbo flex tester which is presented in the side picture given here that actually makes the flexing or that rotates. So, that crease is formed and then it is in opposite direction to enable the prediction and end use performance of the material which is likely to be affected by flexing. For example, formation of pinholes and breaks in the region of the creases. The Galbo flex tester simulates the creasing and flexing action which many films may be subjected to to in use.

 Properties such as water vapour transmission rate can then be measured on film samples before and after flexing on the Galbo flex tester. The another important property is blocking. Blocking is the tendency of two adjacent layers of film in intimate contact with nearly complete exclusion of air to stick together. As for example, when two films are stacked in sheets or compacted rolls temperature or pressure or both can induce or change the degree of adhesion of the surface. It can also make bags made from lay flat film difficult to to open.

 Blocking is also affected by static charges, surface treatment such as printing pre treatment and storage conditions. Anti-blocking additives are often added to the film to reduce the tendency to blocking. These act by diffusing to the surface and forming nonadherent layers. The degree of blocking is determined by the force required to separate the two layers of blocked film. When the force is applied perpendicularly to the surface of the the film.

 Now the barrier properties, the barrier properties of plastics indicate their resistance to absorption and diffusion of substances such as gases and flavour and aroma compounds. The solution and transport behaviour of low molecular weight substances in plastics has become increasingly important in recent years with the wide spread and expanding use of polymer films and rigid plastics for food packaging. The selection or development of plastics for food packaging applications with stringent design specifications relating to their solution and diffusion behaviour requires knowledge and appreciation of the many factors which affect those phenomena. Unfortunately there are many examples of food packaged with an apparent lack of proper consideration of the effects of the end use environment on properties or of laminations imposed on performance due to unfavourable solution or transport characteristics. Plasticization of polymers, absorption of ambient vapours or liquids resulting in a decrease in mechanical properties and the loss of components for example, carbon dioxide, flavour compounds and so on from a beverage in a plastic bottle are just two of many examples which could be cited.

 The protection of foods from gas and vapour exchange with the environment depends on the integrity of packages including their seals and closures and on the permeability of the packaging materials themselves. There are two processes by which gases and vapours may pass through polymeric materials, the first a pore effect in which the gases and vapours flow through microscopic pores, pin holes and cracks in the material. The second a solubility diffusion effect in which the gases and vapours dissolve in the polymer at one surface diffuse through the polymer by virtue of a concentration gradient and evaporate at the other surface of the polymer. This solution diffusion process also known as activated diffusion is described as true permeability. Sufficiently thin most polymer exhibit both forms of permeability, porosity falls very sharply as the thickness of the polymer is increased reaching virtually zero with many of the thicker types of commercially available materials.

 True permeability however, varies inversely as the thickness of the material and hence cannot be effectively eliminated merely by increasing the material thickness. Unlike metal, and glass packages, plastic packages are permeable and the concept of permeability is normally associated with the quantitative evaluation of the various properties of the plastics. A plastic that is a good barrier has a low permeability. This section is concerned with aspects of the solution, diffusion and permeation of gases and vapours that is commonly known as permeates in effectively non-porous polymeric materials. Under steady state conditions a gas or vapour will diffuse through a polymer at a constant rate if a constant pressure difference is maintained across the polymer.

 The diffusive flux J of a permeant in a polymer can be defined as the amount passing through a plane or surface of unit area normal to the direction of flow during unit time as follows. J is equal to Q by area into time where Q is the total amount of permeant which has passed through an area of A during time t. The relationship between the rate of permeation and the concentration gradient is one of direct proportionality and is embodied in Fick's first law. J is equal to minus D delta C by delta x where J is the flux or rate of transport per unit area of permeant through the polymer. C is the concentration of the permeant, D is defined as the diffusion coefficient, delta C divided by delta x is the concentration gradient of the permeant across a thickness of delta x.

 D reflects the speed at which the permeant diffuses through the polymer. It is a function of temperature and may be a function of concentration. Equation 3 can be used to calculate the steady state rate of diffusion assuming that D is constant and the concentration is a function only of the geometric position inside the polymer. A wide range of values for D in polymers are reported from 10 to the power minus 19 to 10 to the power minus 9 meter square per second. By way of comparison D in liquids is around 10 to the power minus 9 meter square per second and in gases around 10 to the power minus 5 meter square per second.

 When a steady state of diffusion has been reached J equal to constant and equation 3 can be integrated across the total thickness of the polymer x and between the two concentrations assuming D to be constant and independent of C . The J is equal to minus D C 2 minus C 1 divided by x. This expression can be rewritten by substituting for J using formula 2. This enables calculation of Q the quantity of permeant diffusing through a polymer of area A in time t is given by equation 5 that is Q is equal to D into C 2 minus C 1 into area into time divided by thickness x. When the permeant is a gas it is more convenient to measure the vapor pressure P which is at equilibrium with the polymer rather than measure the actual concentration.

 At sufficiently low concentrations Henry's law applies and C can be expressed as C is equal to S into P where S is the solubility coefficient of the permeant in the polymer. S reflects the amount of permeant in the polymer by combining equation 5 and 6 that is represented by equation 7 that is Q is equal to $D S$ minus $P 2$ minus $P 1$ into area into time divided by x. The product D S is referred to as the permeability coefficient or constant and is presented by the symbol P, P is equal to D S. Thus the permeability coefficient is the product of a kinetic term D which reflects the dynamics of the permeant polymer system and of a thermodynamic term S which depends on the penetrant polymer interactions. P represents the a is with which a gas permeates through a polymer when subjected to a pressure gradient.

So, P is equal to Q into x divided by a into t into P 1 minus P 2 which will be reduced to or rewritten as Q by t is equal to P by x into a into delta P. The term P by x is called the permeance and is represented by the symbol R. Permeance is not a property of the material, but a performance evaluation indicator. There are four assumptions made in the earlier simple treatment of permeation. The first diffusion is at steady state, second the concentration distance relationship through the polymer is linear.

Third diffusion takes place in one direction only that is through the film with no net diffusion along or across it. And fourth both D and S are independent of the concentration. Although the chemical structure of a polymer can be considered to be the predominant factor which controls the magnitude of P. It also varies with the morphology of the polymer and depends on many physical factors such as density, crystallinity and orientation. The permeability coefficient defined earlier is independent of thickness because the thickness is already accounted for in the calculation of P.

 However, the total amount of protection afforded by unit area of a barrier material that is the permeance P by x approaches 0 only asymptotically. Consequently, as polymer thickness x is increased beyond a certain value it becomes uneconomical to increase it further to obtain lower permeability. Permeation through pores the presence of pores in a

plastic food package is generally considered undesirable and pores or channels leaks are sometimes found in defective seals as a result of faulty heat sealing of plastic films. Numerous micro pores are often present in very thin homogeneous films, but incorporation of such films into a laminate package generally cancels micro porosity. Pores, micro holes and cracks not only allow mass transfer between the interior of a package and the ambient environment, but also permit micropenetration into the package with some bacteria penetrating holes as small as 0.

4 micrometer in diameter. Microscopic defects are common in metallized films even although the metallic coating is generally considered impermeable to a small molecules such as gases, vapor, flavors and also light due to opacity. The permeation through pores these pin holes are created in the metallic layer during manufacture due to presence of anti block and dust particles or aluminum aggregates as well as during the packing and or transportation of package foods. Many small defects lead to a higher permeability than a small number of large defects for the same whole area of defects. The better the gas barrier properties of the packaging material, the more significant is the relative increase in permeability due to leaks. The factors for converting P from various units into barriers are presented in table 1 and broadly representative permeability coefficients of various polymer materials and permeants at 25 degree Celsius at 0 percent relativity are given in table 2.

The different polymers like linear low density polyethylene, low density polyethylene, high density polyethylene etc and the permeates are oxygen, carbon dioxide, nitrogen, sub dioxide and water vapor. The permeability coefficient units D has dimensions of length square per unit time and usually expressed as centimeter squares per second. The dimensions used for P and S are much more varied and a source of much confusion. Consideration of equation 9 shows the dimensions of P to be the P is equal to quantity of permeant under stated conditions into thickness divided by area into time pressure drop across polymer. Let us understand this thing with some example, what is the permeability coefficient of SDPE to sulfur dioxide in MLSTP standard temperature pressure meter square per day per atmospheric pressure.

The answer the from table 2 just now we have seen the table 2 from table 2 the P is 5.7 bar which is equal to 5.7 into 10 to the power 10 milliliter that SDPE centimeter square per second per mercury pressure. The conversion factor from table 1 is 3.86 into 10 to the power minus 14. So, this must be divided into the permeability coefficient obtained from table 2 then P is equal to 5.7 into 10 to the power minus 10 divided by 3.86 into 10 to the power minus 14 which is equal to 1.48 into 10 to the power 4 milliliter at standard temperature pressure milli meters per meters square per day per atmospheric pressure. Therefore, to be a good all round barrier material the polymer must possess the following

properties.

Some degree of polarity which is found in nitrile, chloride, fluoride, acrylic or ester groups. High chain stiffness, high chain stiffness, high chain stiffness inertness to the permeant. Many polymers particularly those containing polar groups can absorb moisture from the atmosphere or from liquids in contact with the polymer. This has the effect of swelling or plasticizing the polymer and reducing the barrier properties. Close chain to chain packing ability brought about by molecular symmetry or order crystallinity or orientation.

Linear polymers with a simple molecular structure are used to produce the polymer, lead to good chain packing and lower permeant permeability than polymers whose backbone contains bulky side groups leading to poor packing ability. The higher the degree of crystallinity the lower the permeability because the crystalline regions are relatively impermeable compared with the amorphous regions. Some bonding or attraction between chains cross linking of polymer chains restricts their mobility and thus decreases their permeability mainly due to the decrease in the diffusion coefficient. For example, in case of polyethylene one cross link about every 30 monomer units leads to a having of the diffusion coefficient. The effect of cross linking is more pronounced for large molecular sized sized permeates.

At high T g and below T g the segments have little mobility and there is also a reduction in free volume. Thus not only there are less voids, but in addition a diffusing molecule will have a much tortuous path through the polymer. Therefore, if a polymer has a high T g then it is likely that its temperature of use will be below its T g and it will be consequently have improved barrier properties. Thank you that's all for today.