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Paper Title: Food packaging technology

Module – 10: Structure and properties of plastic polymers

10.1 Introduction

Different types of plastics are used for different purposes based on the characteristics of plastics and type of product. Some of the plastics are discussed hereunder that can be used in food packaging.

10.2 Polyethylene (PE)

PE is structurally the simplest plastic and is made by addition polymerization of ethylene gas in a high temperature and pressure reactor. Low, medium and high density resins are produced, depending on the conditions (temperature, pressure and catalyst) of polymerization. The processing conditions control the degree of branching in the polymer chain and therefore the density and other properties of films and other types of packaging. Polyethylenes are readily heat sealable. They can be made into strong, tough films, with good moisture and water vapour barrier properties. They are not high barrier to oils and fats or gases such as carbon dioxide and oxygen compared with other plastics, although barrier properties increase with density. The heat resistance is lower than that of other plastics used in packaging, with a melting point of around 120°C. The melting point increases as the density increases.

PE was first used as an insulator in the 1940s. PE films are highly susceptible of generating a static charge and need to have antistatic, slip agents and anti-blocking compounds added to the resin to assist film manufacturing, conversion and use. It is the most widely used and is cost effective.

10.2.1 Low density polyethylene (LDPE)

LDPE is easily extruded as a tube and blown to stretch it by a factor of three times the original area. It is commonly manufactured around 30 µm (20 or 25 µm is also possible) within a density range 0.910–0.925 g cm^{-3}.

The films can be coloured by blending pigment with the polymer prior to extrusion where extruders have more than one die. Two or more layers of the same material or coextruded films comprised of layers of different plastic materials can also be produced. With three extruders, it is possible to produce a film where, for example, a moisture-sensitive polymer, EVOH, is sandwiched between protective layers of PE. EVOH provides a gas and odour barrier, and the PE offers good heat-sealing properties and a substrate for printing.

PE film melts at relatively low temperatures and welds to itself when cut with a hot wire, or blade, to form effective seals. For packaging, it is possible to use either premade bags or form/fill/seal machines using flat film in reel form. A major use of white pigmented LDPE film is for making bags for holding frozen vegetables.

By laminating to other substrates with adhesives, or extruding the PE polymer onto another material, or web, it is possible to make strong sachets, pouches and bags with good seal integrity, as the PE flows to fill holes in the sealing area or around contaminants in the seal.

10.2.2 Linear low-density polyethylene (LLDPE)

LLDPE film has a density range similar to that of LDPE. It has short side chain branching and is superior to LDPE in most properties such as tensile and impact strength and also in puncture resistance. A major use has been the pillow pack for liquid milk and other liquid foods.

10.2.3 Medium-density polyethylene (MDPE)

MDPE film is mechanically stronger than LDPE and therefore used in more demanding situations. LDPE is coextruded with MDPE to combine the good sealability of LDPE with the toughness and puncture resistance of MDPE, e.g. for the inner extrusion coating of sachets for dehydrated soup mixes.

10.2.4 High-density polyethylene (HDPE)

HDPE is the toughest grade and is extruded in the thinnest gauges. This film is used for boil-in-the-bag applications. To improve heat sealability, HDPE can be coextruded with LDPE to achieve peelable seals where the polymer layers can be made to separate easily at the interface of the co-extrusion. HDPE film is available with either TD monoaxial orientation or biaxial orientation.

HDPE is injection moulded for closures, crates, pallets and drums, and rotationally moulded for intermediate bulk containers (IBCs). A major application of HDPE is for blow moulded milk containers with a capacity 0.5–3 l.

10.3 Polypropylene (PP)

PP is an addition polymer of propylene formed under heat and pressure using Zieger-Natta type catalysts to produce a linear polymer. PP is a harder and denser resin than PE and more transparent in its natural form. The usage of PP developed from the 1950s onwards. PP has the lowest density and highest melting point of all the high volume usage thermoplastics and has a relatively low cost. It can be processed in many ways and has many food packaging applications in both flexible film and rigid form.

The high melting point of PP (160°C) makes it suitable for applications where thermal resistance is needed, for example in hot filling and microwave packaging. PP may be extrusion laminated to PET or other high-temperature resistant films to produce heat-sealable webs which can withstand temperatures of up to 115–130°C, for sterilizing and use in retort pouches.

PP is chemically inert and resistant to most commonly found chemicals, both organic and inorganic. It is a barrier to water vapour and has oil and fat resistance.

Orientation increases the versatility of PP film. Oriented PP (OPP) or biaxially oriented PP (BOPP) film was the first plastic film to successfully replace regenerated cellulose film (RCF) in major packaging applications such as biscuit packing. Acrylic-coated OPP has good runnability, including heat sealing, on packing machines, designed for RCF, though improved temperature control of the heat-sealing equipment is required.

OPP film is produced in widths of up to 10 m or more to achieve cost-effective production. The limiting factors in production are either extrusion capacity for the thicker films or winding speed for the very thin films.

The range of food products packed in PP films include biscuits, crisps (chips) and snack foods, chocolate and sugar confectionery, ice cream and frozen food, tea and coffee. Metalized PP film can be used for snacks and crisps (chips) where either a higher barrier or longer shelf life is required.

Paperboard can be extrusion coated with PP for use as frozen or chilled food trays which can be heated in microwave and steam-heated ovens. Major food applications of PP are for injection-moulded pots and tubs for yoghurt, ice cream, butter and margarine. It is also blow-moulded for bottles and wide mouth jars. PP is widely used for the injection moulding of closures for bottles and jars.

It is used in thermoforming from PP sheet, as a monolayer, for many food products such as snacks, biscuits, cheese and sauces. In co-extrusions with PS, EVOH and PE it is used for the packaging of several types of food product including those packed aseptically, by hot filling, and in microwaveable and retortable packs.

10.4 Polyethylene terephthalate (PET or PETE)

When terephthalic acid reacts with ethylene glycol and polymerises, the result is PET.

PET can be made into film by blowing or casting. It can be blow moulded, injection moulded, foamed, extrusion coated on paperboard and extruded as sheet for thermoforming. PET can be made into a biaxially oriented range of clear polyester films produced on essentially the same type of extrusion and Stenter-orienting equipment as OPP. Film thicknesses range from thinner than 12 μm for most polyester films to around 200 μm for laminated composites.

PET melts at 260°C, and due to the manufacturing conditions does not shrink below 180°C. Therefore, PET is ideal for high-temperature applications using steam sterilisation, boil-in-the-bag and for cooking or reheating in microwave or conventional radiant heat ovens. The film is also flexible in extremes of cold (−100°C). Heat-sealable versions are available, and it can also be laminated to PE to give good heat-sealing properties. Coating with PVdC give a good gas barrier and heat-sealing capability.

PET is a medium oxygen barrier but becomes a high barrier to oxygen and water vapour when metalized with aluminium. This is used for vacuumised coffee and bag-in-box liquids, where it is laminated with EVA on both sides to produce highly effective seals. It is also used in snack food flexible packaging for products with a high fat content requiring barriers to oxygen and ultra violet (UV) light. Metalized PET, either as a strip or as a flexible laminate, is used as a susceptor in microwaveable packaging.

Reverse printed PET film is used as the external ply on FFS pouches where it provides a heat-resistant surface for contact with the heat-sealing bars. The amorphous cast grades can be used as the bottom web in formed applications which are lidded with a heat-sealable grade of PET. These packs can be reheated in microwave and conventional ovens.

PET film is also used as the outer reverse-printed ply in retort pouches, providing strength and puncture resistance, where it is laminated with aluminium foil and either PP or HDPE. PET can be oxide coated with SiO_2 to improve the barrier, whilst remaining transparent, retortable and microwaveable.

Paperboard is extrusion coated with PET for use as ready meal trays which can be reheated in microwave or conventional radiant heat ovens, i.e. dual ovenable. The PET coated side of the paperboard is on the inside of the tray which is erected by corner heat sealing.

PET is the fastest growing plastic for food packaging applications as a result of its use in all sizes of carbonated soft drinks and mineral water bottles which are produced by injection stretch blow moulding. PET bottles are also used for edible oils, as an alternative to PVC.

10.5 Polycarbonate (PC)

PC is a polyester containing carbonate groups in its structure. It is formed by the polymerisation of the sodium salt of bisphenolic acid with phosgene. It is glass clear, heat resistant and very tough and durable. PC is mainly used as a glass replacement in processing equipment and for glazing applications. Its use in packaging is mainly for large, returnable/refillable 3–6 litre water bottles. It is used for sterilisable baby feeding bottles and as a replacement in food service. It has been used for returnable milk bottles, ovenable trays for frozen food and if coextruded with nylon could be used for carbonated drinks.

10.6 Ionomers

Ionomers are polymers formed from metallic salts of acid copolymers and possess interchange ionic cross-links which provide the characteristic properties of the family of plastics. The metallic ions can be zinc or sodium and the copolymer is based on ethylene and methacrylic acid. It is clear, tougher than PE, having high puncture strength, and has excellent oil and fat resistance. Hence, it is used for the packaging of products contain essential oils, in the aseptic liquid packaging of fruit juices in cartons, and fat containing products (e.g. snack foods) in sachets. It has excellent heat-sealing properties, leading to increased packing line speeds. It is used in the packaging of meat, poultry and cheese. It is particularly useful in packing product with sharp protrusions.

In food packaging, ionomer films, including coextruded films, are used in laminations and extrusion coatings in all the main types of flexible packaging.

These include:

- vertical and horizontal FFS
- vacuum and MAP packing
- four-side sealed pouches and twin-web pouches with one web thermoformed
- inner ply of paperboard composite cans, e.g. aluminium foil/ionomer
- diaphragm or membrane seals.

Ionomers are used in laminated and coated form with PET, PA, PP, PE, aluminium foil, paper and paperboard.

10.7 Ethylene vinyl acetate (EVA)

EVA is a copolymer of ethylene with vinyl acetate. It is similar to PE in many respects, and it is used, blended with PE, in several ways. The properties of the blend depend on the proportion of the vinyl acetate component. Generally, as the VA component increases, sealing temperature decreases and impact strength, low temperature flexibility, stress resistance and clarity increase. At a 4% level, it improves heat sealability, at 8% it increases toughness and elasticity, along with improved heat sealability, and at higher levels, the resultant film has good stretch wrapping

properties. EVA with PVdC is a tough high-barrier film which is used in vacuum packing large meat cuts and with metalized PET for bag-in-box liners for wine.

Modified EVAs are available for use as peelable coatings on lidding materials such as aluminium foil, OPP, OPET and paper. They enable heat sealing, resulting in controllable heat seal strength for easy, clean peeling. These coatings will seal to both flexible and rigid PE, PP, PET, PS and PVC containers.

Modified EVAs are also used to create strong interlayer tie bonding between dissimilar materials, e.g. between PET and paper, LDPE and EVOH. EVA is also a major component of hot melt adhesives, frequently used in packaging machinery to erect and close packs, e.g. folding cartons and corrugated packaging.

10.8 Polyamide (PA)

PA are commonly known as nylon. They were initially used in textiles, but subsequently other important applications were developed including uses in packaging and engineering. Polyamide plastics are formed by a condensation reaction between a diamine and a diacid or a compound containing each functional group (amine). The different types of polyamide plastics are characterised by a number which relates to the number of carbon atoms in the originating monomer. It has mechanical and thermal properties similar to that of PET and therefore similar applications. PA resins can be used to make blown film, and they can be coextruded.

PA can be blended with PE, PET, EVA and EVOH. It can be blow moulded to make bottles and jars which are glass clear, low in weight and have a good resistance to impact.

Biaxially oriented PA film has high heat resistance and excellent resistance to stress cracking and puncture. It has good clarity and is easily thermoformed, giving a relatively deep draw. It provides a good flavour and odour barrier and is resistant to oil and fat. It has a high permeability to moisture vapour and is difficult to heat seal. These features can be overcome by PVdC coating. They can also be overcome by lamination or co-extrusion with polyethylene, and this structure is used as the bottom thermoformable web, i.e. deep drawn, for packing bacon and cheese in vacuum packs or in gas-flushed packs (MAP or modified atmosphere packaging). The film can also be metalized.

PA film is used in retortable packaging in structures such as PA/aluminium foil/PP. The film is non-whitening in retort processing. PA is relatively expensive compared with PE, but as it has superior properties, it is effective in low thicknesses.

10.9 Polyvinyl chloride (PVC)

If one of the hydrogen atoms in ethylene is replaced with a chlorine atom, the resultant molecule is called vinyl chloride monomer (VCM). Addition polymerization of vinyl chloride produces PVC.

Rigid Unplasticized PVC (UPVC) is used for transparent or coloured compartmented trays for chocolate assortments and biscuits. It is used with MAP for thermoformed trays to pack salads, sandwiches and cooked meats.

Most PVC films are produced by extrusion, using the bubble process. It can be oriented to produce film with a high degree of shrinkability. Up to 50% shrinkage is possible at quite low temperatures. The film releases the lowest energy of the commonly used plastic films when it is heat shrunk around products. It is plasticised, and the high stretch and cling make it suitable for

overwrapping fresh produce, e.g. apples and meat in rigid trays using semi-automatic and manual methods.

Printed PVC film is used for heat-shrinkable sleeve labels for plastic and glass containers. It is also used for tamper-evident shrink bands. Thicker grades are thermoformed to make trays which, after filling, are lidded with a heat seal-compatible top web.

PVC has excellent resistance to fat and oil. It is used in the form of blow moulded bottles for vegetable oil and fruit drinks. It has good clarity. As a film, it is tough, with high elongation, though with relatively low tensile and tear strength. The moisture vapour transmission rate is relatively high, though adequate for the packaging of mineral water, fruit juice and fruit drinks in bottles. PVC softens, depending on its composition, at relatively low temperatures (80–95°C). PVC easily seals to itself with heat, but heat sealing with a hot wire has the disadvantage of producing HCl gas.

The permeability to water vapour and gases depends on the amount of plasticizer used in manufacture. UPVC is a good gas and water vapour barrier, but these properties decrease with increasing plasticiser content. There are grades which are used to wrap fresh meat and fresh produce, where a good barrier to moisture vapour retards weight loss, but the permeability to oxygen allows the product to *breathe*. This allows fresh meat to retain its red colour and products such as fruits, vegetables and salads to stay fresh longer by reducing the rate of respiration, especially when packed in a modified atmosphere (MAP).

10.10 Polyvinylidene chloride (PVdC)

PVdC is a copolymer of vinyl chloride and vinylidene chloride – the latter forms when two hydrogen atoms in ethylene are replaced by chlorine atoms.

PVdC is heat sealable and is an excellent barrier to water vapour and gases and to fatty and oily products. As a result of the high gas and odour barrier, it is used to protect flavour and aroma sensitive foods from both loss of flavour and ingress of volatile contaminants. It is used in flexible packaging in several ways:

Monolayer film: A well-known application is the Cryovac range introduced by W.R. Grace and now operated by the Sealed Air Corporation. This includes poultry packing where hot water shrinkable bags are used to achieve a tight wrap around the product. The film can be used in the form of sachets but is less likely to be cost effective compared with other plastic films – some of which may incorporate PVdC as a coating. An interesting use is as sausage and chubb casing.

Coextrusions: PVdC is often used in coextrusion, where, today, extruders incorporate three, five and even seven extrusion layers to meet product protection and packaging machinery needs cost effectively.

Coatings. These may be applied using solutions in either organic solvents or aqueous dispersions to plastic films such as BOPP and PET, to RCF and to paper and paperboard.

Hence, PVdC is a widely used component in the packaging of cured meats, cheese, snack foods, tea, coffee and confectionery. It is used in hot filling, retorting, low-temperature storage and MAP as well as ambient filling and distribution in a wide range of pack shapes.

10.11 Polystyrene (PS)

PS is an addition polymer of styrene, a vinyl compound where a hydrogen atom is replaced with a benzene ring. PS has many packaging uses and can be extruded as a monolayer plastic film, coextruded as a thermoformable plastic sheet, injection moulded and foamed to give a range of pack types. It is also copolymerised to extend its properties.

It is less well known as an oriented plastic film, though the film has interesting properties. It has high transparency (clarity). It is stiff, with a characteristic crinkle, suggesting freshness, and has a deadfold property. The clear film is used for carton windows, and white pigmented film is used for labels. The film is printable. It has a low barrier to moisture vapour and common gases, making it suitable for packaging products, such as fresh produce, which need to breathe.

PS is easily processed by foaming to produce a rigid lightweight material which has good impact protection and thermal insulation properties. It is used in two ways. The blown foam can be extruded as a sheet which can be thermoformed to make trays for meat and fish, egg cartons, a variety of fast food packs such as the clam shell-shaped container, as well as cups and tubs. Thin sheets can be used as a label stock. The foam can also be produced in pellet or bead form which can then be moulded with heat and pressure. This is known as expanded polystyrene or EPS. It can be used as a transit case for fresh fish, with thick walls for insulation.

PS so far described is general purpose polystyrene. The main disadvantage as a rigid or semi-rigid container is the fact that it is brittle. This can be overcome by blending with styrene butadiene copolymer, SB or SBC, an elastomeric polymer. The blend is known as high-impact polystyrene or HIPS.

Blending produces a tougher material. It is translucent and is often used in a white pigmented form. The sheet can be thermoformed for short shelf life dairy products.

HIPS is also used in multilayer sheet extrusion with a variety of other polymers, each of which contributes to the protection and application needs of the product concerned. Other polymers which may be used in this way with HIPS include PE, PP, PET, PVdC and EVOH. The food products packed with these materials include dairy products such as cream and yoghurt-based desserts, UHT milk, cheese, butter, margarine, jam, fruit compote, fresh meat, pasta, salads etc. Many of these products are packed aseptically on thermoform, fill and seal machines.

10.12 Ethylene vinyl alcohol (EVOH)

EVOH is a copolymer of ethylene and vinyl alcohol. It is related to polyvinyl alcohol (PVOH), which is a water-soluble synthetic polymer with excellent film-forming, emulsifying and adhesive properties. It is a high-barrier material with respect to oil, grease, organic solvents and oxygen. It is moisture sensitive and, in film form, is water soluble. PVOH itself has packaging applications in film form but not in food products, and it is used as a coating for BOPP.

EVOH was developed to retain the high-barrier properties of PVOH. It is also an excellent barrier to oxygen and is resistant to the absorption and permeation of many products, especially those containing oil, fat and sensitive aromas and flavours. Though it is moisture sensitive to a much lesser degree than PVOH, it is still necessary to *bury* it in multilayered coextruded structures, such as film for flexible packaging, sheets for thermoforming and in blowmoulded bottles, so that it is not in contact with liquid.

The other polymers used depend on the application, i.e. the food product and type of pack. PS/EVOH/PS and PS/EVOH/PE sheets are used for processed cheese, pâtè, UHT milk and milk-

based desserts and drinks. It is also used for MAP of fresh meat and for pasta, salads, coffee and hot filled processed cheese, including portion packed cheese and fruit compote.

A higher-barrier sheet can be constructed with PP/EVOH/PP for pasterizable and retortable products such as fruit, pâté, baby food, sauces like ketchup and ready meals, some of which are reheated by microwave. Coextruded film applications can involve EVOH with nylon, LLDPE and ionomer with food products such as bag-in-box wine, processed and fresh meat.

Extrusion lamination can involve EVOH with PET, LDPE and LLDPE for coffee, condiments and snacks. It is used with PET and PP for tray lidding material. Extrusion lamination of paperboard with EVOH and PE is used for aseptically packed UHT milk and fruit juices where the EVOH layer provides an oxygen barrier as a replacement for aluminium foil. In blow moulding, EVOH is used with PP for sauces, ketchup, mayonnaise and cooking oil and with HDPE for salad dressings and juices. Ketchup and mayonnaise bottles based on EVOH are squeezable.

Small tubes made by profile coextrusion are used for condiments by incorporating EVOH into structures with LDPE and LLDPE. EVOH is an important polymer in many processing applications providing protection for many types of food product.

10.13 Fluoropolymers

Fluoropolymers or fluoroplastics are high-performance polymers related to ethylene where some or all of the hydrogen atoms are replaced by fluorine, and in the packaging polymer a hydrogen is also replaced by a chlorine atom to produce polychlorotrifluoroethylene (PCTFE).

It has the highest water vapour barrier of all the commercially available packaging polymers, is a very good gas barrier and offers high resistance to most chemicals at low temperatures. In many applications, it is a suitable replacement for aluminium foil. It is available as a film or sheet. It is transparent, heat sealable and can be laminated, thermoformed, metalized and sterilized.

It is relatively expensive and is best known as a thermoformable blister pack material laminated with PVC for pharmaceutical tablets. Food packaging applications are possible but are not highlighted at the present time. Polytetrafluoroethylene (PTFE), better known as Teflon, is a high melting point, inert and waxy polymer. It is used in the form of tape and coatings on packaging machines to reduce adhesion, where that could be a problem, e.g. heat seal bars, and to reduce friction where packaging materials move over metal surfaces.