PERP Program – New Report Alert

May 2005

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Specialty LDPE Copolymers (03/04S9)***.

Introduction

The materials covered by this report are those ethylene copolymers that can be made in high pressure polyethylene plants. The largest volume copolymer is vinyl acetate copolymer (EVA) containing 9 percent or more vinyl acetate. EVA copolymers with less than 9 percent vinyl acetate have largely been commoditized and are not considered in this report. The practical upper limit is 40 percent vinyl acetate for the high pressure process.

Other high pressure copolymers covered in this report are ethylene ethyl acrylate (EEA), ethylene n-butyl acrylate (EBA) and ethylene methyl acrylate (EMA) at all percentage levels.

If an acid is used instead of an ester as a comonomer, the so-called acid copolymers are made. These have high bond-strength to metals, but tend to be corrosive. The acid copolymers covered in this report are ethylene acrylic acid (EAA) and ethylene methacrylic acid (EMAA) at all comonomer levels.

If the acid copolymers are neutralized with sodium or zinc bases, ionomers are produced. The original ionomer was Surlyn made by DuPont from EMAA, but the patents have now expired and others are now making ionomers based on EAA. Ionomers are covered in this report as well.

Ethylene copolymers, derived from the polymerization of ethylene and a comonomer (e.g., vinyl acetate, ethyl acrylate, acrylic acid or methyl acrylate), extend the performance range of the broad class of high pressure polyethylene resins. The inclusion of a comonomer reduces the crystallinity of the copolymer, as well as its melting point, resulting in improved flexibility, impact strength and heat sealing characteristics.

The ethylene copolymers differ from conventional low density polyethylene (LDPE) in several respects. Properties of the copolymers are strongly dependent on comonomer type and content and less dependent on density. In general, ethylene copolymers offer better impact strength, flexibility, low temperature properties and resistance to environmental stress cracking than LDPE, but exhibit lower melting points and more narrow processing ranges. Thus flexibility is achieved without the addition of potentially migratory plasticizers.

The specialty LDPEs covered in this report compete against a range of other polyethylene based products. This is illustrated in Figure 1.

Figure 1
Physical Property Comparison

Product	Puncture	Toughness	Tear	Optics	Organoleptics	Vapor barrier	Hot tack	Sealing	Stiffness	Processability
LDPE	●	●	■	■	▲	■	●	■	■	▲
LLDPE	■	■	▲	■	■	■	■	■	■	●
metallocene LLDPE	▲	▲	▲	■	▲	■	▲	■	■	●
metallocene VLDPE	▲	▲	■	▲	▲	■	▲	▲	■	●
HDPE	●	■	●	●	■	▲	●	●	▲	■
High EVA* (over 9%)	■	■	■	▲	●	●	●	▲	●	■
EAA*	■	■	●	●	●	●	■	▲	■	▲
EnBA*	●	●	●	■	●	●	●	▲	●	●
EMA*	●	●	●	●	●	●	●	▲	●	▲
Ionomers*	▲	▲	■	▲	●	●	▲	▲	■	■

● Lowest Range ■ Intermediate Range ▲ Highest Range

*Covered in this report
Source: ExxonMobil

Q404_00101.0004.4116-2.ppt

Ethylene Vinyl Acetate (EVA)

EVA copolymers make up a family of products with wide property variation. They range from thermoplastic products, similar to LDPE, to rubber-like products. EVA is produced by the random copolymerization of ethylene and vinyl acetate in predetermined ratio. The presence of VA reduces the crystallinity as the large acetoxy group distorts the chain structure. The copolymer is made using peroxide initiators in a high pressure reactor as for LDPE, and thus similar chain branching occurs to give long and short alkyl chains which also reduce the crystallinity. At about 50 percent by weight of VA, all polymer crystalline structure is completely destroyed to give an amorphous rubber.

The EVA molecular weight distribution (MWD) depends on the process used; thus tubular reactors give broader MWD resins than autoclaves. MWD can affect the crystallinity for a given vinyl acetate content and the processability. Tensile strength, stiffness and hardness are greater for narrow MWD resins, but compatibility is not affected as this is a function of the number of polar acetoxy groups. Thus, MWD is important to the film and extrusion coating sector, but less important to the adhesives formulator. There is greater material competition in the adhesives business as both tubular and autoclave reactor operators can compete equally.

The stiffness of EVA varies with VA content. However, beyond about 60 percent VA, the stiffness rises sharply as pure vinyl acetate is a glass-like substance at room temperature. The practical limit for "mechanical" uses of EVA is about 20 percent VA content; however, for adhesives higher levels of VA are used.

Besides the vinyl acetate content, the next important variable in EVA resins is molecular weight. The high pressure process is best suited for VA levels of up to 35 percent by weight. Above this level the vinyl acetate acts increasingly as a telogen or chain stopper, thus making it difficult to make high average molecular weight resins (measured as low melt flow index). Thus, for high VA levels a low pressure solution process is more appropriate.

The addition of vinyl acetate to ethylene polymers reduces the crystallinity and increases the polarity of the resulting EVA copolymer by comparison to homopolymer LDPE. Reduced crystallinity results in improved flexibility, clarity, stress-crack and flex-crack resistance, low temperature flexibility and impact strength. However, the EVA copolymers exhibit reduced tensile strength, hardness, oil and grease resistance, melt point, heat seal temperature and dielectric properties versus the homopolymers, as well as greater permeability to gases and water vapor.

The polarity of the VA molecule makes the copolymers receptive to high filler loadings and to combination with tackifiers and other adhesive components. Fillers and additives are used to modify EVA properties for such applications as wire and cable jacketing, carpet backing, sound deadening foams and adhesives.

Unlike ethylene copolymers, VA copolymer properties are not directly described by density, but rather density is a function of comonomer content and is thus affected by resin crystallinity. As vinyl acetate level is increased, EVA copolymers exhibit higher density. Increased vinyl acetate content, in general, improves flexibility, elongation, adhesion, weathering properties and solubility in organic solvents. Thus, high VA level copolymers are typically used in adhesive applications, while lower vinyl acetate containing copolymers, whose tensile moduli and surface hardness are greater, find greatest use in films, profile extrusions and injection molding.

The flexibility imparted by the vinyl acetate gives EVA copolymers elastomer-like properties. With elongation values ranging from 400 to over 1,000 percent, EVA polymers retain flexibility to temperatures as low as –100°C. Their ozone resistance is superior to most rubbers and the EVA copolymers may be cross-linked to improve compression set properties. Cross-linking also enhances abrasion resistance, toughness and heat deflection temperature. Cross-linking may be achieved either by exposure to radiation or by chemical means, such as the use of peroxide cross-linking agents.

The melt flow rate or melt index of an EVA copolymer describes the viscosity of the material in the melt and its molecular weight. As melt index increases, the copolymer exhibits improved flexibility, with concomitant declines in tensile strength, thermal stability and hardness. High melt flow rate grades are preferred for injection molding, since these grades fill mold cavities and solidify rapidly. Conversely, for extrusion processes, low melt flow rate grades are preferred to give the fabricator greater process flexibility and polymer melt strength before solidification.

EVA copolymers offer versatility to the fabricator in the range of processing techniques that may be employed. In addition to blown and cast films, injection molding and profile extrusions of neat resin, EVA's can be foamed by either physical (nitrogen gas) or chemical (e.g., azodicarbonamide) means. EVA copolymers may also be blended with other polymers, such as polyolefins and styrene block copolymers, to enhance tear strength, low temperature properties, flexibility and heat seal range, or to reduce cost.

The combination of melt index and vinyl acetate level enables a wide range of properties to be covered, and depending on the application, a compromise has to be struck between these properties. Figure 2 illustrates the direction of the property movements with either molecular weight or vinyl acetate level. The end-use sectors overlap in properties, but Figure 3 shows the typical range of melt index and VA content, by application.

EVA is thermally unstable above 220°C, and so has to be processed with care to avoid breakdown to acetic acid.

As discussed earlier, the higher percent VA resins have a good compatibility with other materials. Thus, EVA is widely used in blends and compounds. The main application is hot melt adhesives (HMA), where the EVA is blended with tackifier and paraffin wax.

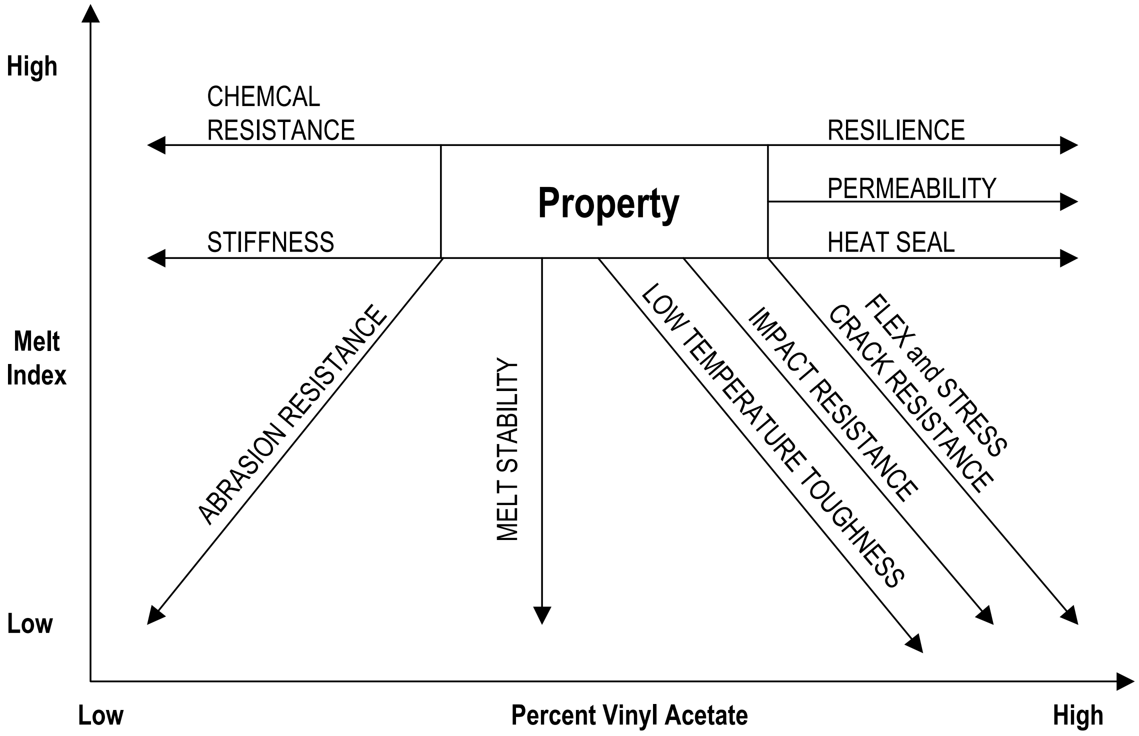
The tackifier improves the adhesion and increases the 'open time' of the formulation. The melt viscosity is lowered by adding microcrystalline waxes or low molecular weight polyethylene to HMA. Wax is added to HMAs to lower viscosity and to cheapen the formulation, but it reduces bond strength and thus wax modified HMAs are used for light duty applications such as packaging and book binding.

A derivative of the HMA is the pressure sensitive adhesive (PSA) containing EVA. No wax or crystalline polymer is used as it reduces the tack.

Other Copolymers

Ethylene methyl acrylate (EMA) is more flexible than LDPE and more 'rubbery'. It has excellent snap back elasticity and its cold resistance is greater than LDPE. However, it is less stable than LDPE and should be processed at 300°F (150°C) maximum. The film has poor optics, good dart drop, low tear strength, low stiffness and good sealability. It adheres well to paper and non-porous materials such as OPP, polyester and PVdC. EMA can be used as a coextrusion tie layer for LDPE, LLDPE, ionomer, PP and even polycarbonate.

Figure 2
Variation of EVA Resin Property with Melt Index and Vinyl Acetate Level



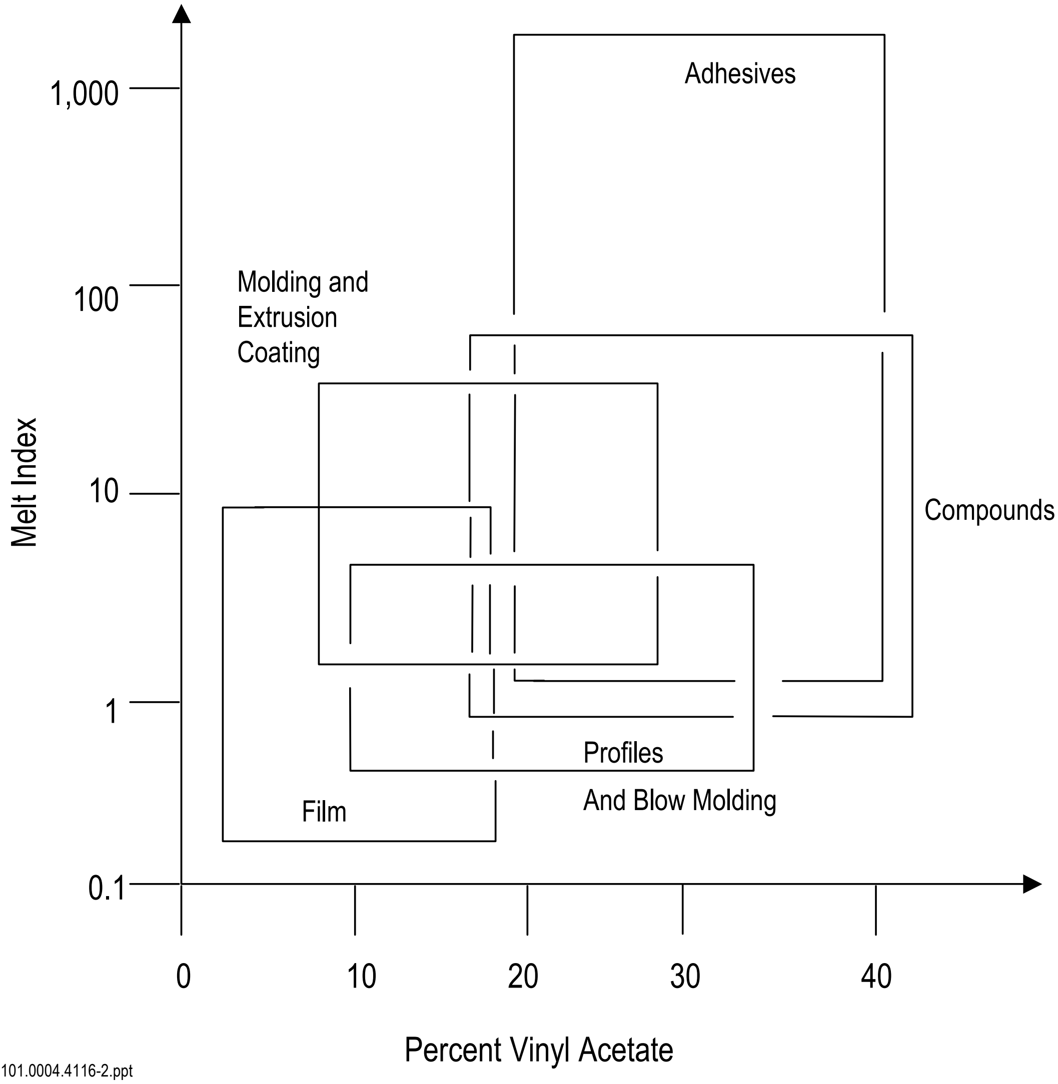
Q404_00101.0004.4116-2.ppt

The main uses for EMA are for medical packaging, disposable gloves, upholstery wrap and cable compounding.

The main use for ethylene ethyl acrylate (EEA) is as a cable compound. EEA competes with EVA in only a few applications as it is superior in terms of heat resistance, flex resistance and low temperature flexibility. However, EEA is not as transparent and is more expensive than EVA. EEA is typically not used in film applications.

While most EEA applications use the copolymer for extruded hose or cable, some high ethyl acryate (30 percent) content resin is used in hot melt adhesives to give better heat resistance than EVA.

Figure 3
EVA Application Range



Q404_00101.0004.4116-2.ppt

EEA is widely processed by injection molding and extrusion. A small amount of EEA is used for blow molding. EEA is more stable than EVA and is less likely to give corrosive decomposition products.

All the ethylene *n*-butyl acrylate (EBA) copolymers are low melt index film resins. Several are sold as compounds with chalk and slip additives for the manufacture of thin 'hygiene' films. EBA is a very tough film, even at low temperatures, and is probably the best film for the packaging of frozen foods. However, it is more expensive than EVA and tends to lose this market to high percent comonomer EVA. The tensile strength of EBA is above that of even a fractional melt index LDPE, and the flexibility is greater. However, poor haze and gloss limit the use of EBA to functional films, not decorative ones.

The ethylene acrylic acid (EAA) copolymers, containing 3.5 to 9 percent acrylic acid, are superior to LDPE in strength, toughness, hot tack and adhesion. The two main uses for EAA are as film for blister packing, and as an extrusion coating tielayer between aluminum foil and other polymers. Elongation goes up with increased comonomer content, but optical properties deteriorate. Tensile strength and dart impact decrease with an increase in melt index.

Ethylene methacrylic acid (EMAA) copolymers, at low levels of methacrylic acid, are flexible materials similar to LDPE. As the acid level is increased, they become more transparent to about 6 mole percent. At 8 to 10 mole percent they are quite transparent and tough, but above 10 mole percent they are brittle, glassy solids.

EMAA competes in some applications with the neutralized form (ionomer). EMAA has slightly better sealing properties than EAA and is less corrosive, as methacrylic acid is milder than acrylic acid.

Ionomers

DuPont founded the ionomers business and still dominates it with sodium and zinc neutralized grades based on EMAA. Neutralization of EMAA with a cation (e.g. sodium or zinc) creates a three dimensional network in the ionomer. The ionic crosslinks are responsible for the unique properties of ionomers. The ionic interactions and subsequent polymer properties are dependent on the type of polymer chain, ionic content, type of ionic moiety, degree of neutralization and type of cation.

All the ionomers are more transparent than EMAA, the sodium ionomers being more transparent than the zinc based ones. This improved transparency is due to the high melt viscosity hindering the formation of large crystallites, thus reducing internal haze. The ionic regions nucleate small crystallites and so surface gloss is high and ionomer films have high ‘sparkle’.

The high melt strength of ionomers means that they can be used for blow molding and drawn down to thin films without breaking. High melt strength prevents pinholes in thin coatings and prevents fiber ends puncturing the molten web of ionomer as it is being laid down on the paper. Thus ionomers are specified for critical coating applications such as juice pouches where any leakage of the acid juice would attack the aluminum foil.

LDPE Copolymer Production

The plant modifications necessary to produce the copolymers depend on the level of comonomer in the final copolymer and the melt index range to be produced. Besides the obvious comonomer feed tanks and injection units, the discharge extruder and cutter may need to be modified.

The effect on output of all the changes required to produce LDPE copolymers typically leads to a drop in production of from 10 to 35 percent depending on grade type. Most copolymer producers run campaigns of grades thus minimizing offgrade production.

Economics

Economics were developed for a series of EVA copolymer products (10,18, 28 percent VA content tubular resins, and 10, 18, 28 and 40 percent VA content autoclave resins), plus EEA, EAA, EMA, EMAA and ionomer products. Homopolymer LDPE economics were also prepared as a comparison. These economics assume only a minimal level of additives, notably an anti-oxidant additive package.

The economics assume that the tubular and autoclave reactors are a single train for the given size. Although the capital costs include generous allowances for separate storage and product handling equipment (as opposed to sharing this equipment and raising the chance of contamination), the economics also assume that the facilities modeled are part of larger polyolefin sites, sharing infrastructure such as utilities, roads and rail links and the like.

Some allowance has also been made in the operating rates used to account for the need to run at lower rates for the higher VA content materials.

Commercial Analysis

The report includes demand estimates for various classes of ethylene copolymers in North America, Western Europe, and Japan for the period 2001-2014. Likewise, producers of ethylene copolymers, their capacities, and their product range are provided for the same regions (2004 basis).

= =

Nexant, Inc. (www.nexant.com) is a leading management consultancy to the global energy, chemical, and related industries. For over 38 years, Nexant/ChemSystems has helped clients increase business value through assistance in all aspects of business strategy, including business intelligence, project feasibility and implementation, operational improvement, portfolio planning, and growth through M&A activities. Nexant's chemicals and petroleum group has its main offices in White Plains (New York) and London (UK), and satellite offices worldwide.

These reports are for the exclusive use of the purchasing company or its subsidiaries, from Nexant, Inc., 44 South Broadway, 5th Floor, White Plains, New York 10601-4425 U.S.A. For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: http://www.nexant.com.