

## WHITE PAPER

# AUTOCLAVE LDPE FOR EXTRUSION COATING APPLICATIONS

Dr. Predrag Micic  
Product Development Executive  
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Find out why autoclave technology is superior to tubular technology for the production of extrusion coating resins.  
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The extrusion coating of a substrate such as paper, paperboard, metal foil or plastic film with a thin layer of a polymer—typically low density polyethylene—is an effective way to combine the desired properties of the two materials. The resulting thin multi-layer products are widely used in the packaging industry, or in other industrial uses that require the barrier and sealing properties of a PE layer.

**LDPE is manufactured in either an autoclave reactor or a tubular reactor. LDPE resin made using autoclave technology typically has a larger proportion of high molecular weight polymer, a higher degree of long chain branching and a higher melt strength than resins made using tubular reaction technology. These properties are well suited to extrusion coating operations, and so the market for extrusion coating has a high preference for resins made using the autoclave process.**  
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THE PRODUCTION OF LAMINATED AND COMPOSITE FLEXIBLE MATERIALS USING EXTRUSION COATING TECHNIQUES WAS FIRST ESTABLISHED NEARLY 60 YEARS AGO. SINCE THEN, MORE SOPHISTICATED MATERIALS HAVE BEEN DEVELOPED WITH THE PROPERTIES OPTIMISED TO MEET THE NEEDS OF MODERN PACKAGING AND INDUSTRIAL APPLICATIONS. MOST EXTRUSION COATED PRODUCTS ARE USED TO PACK, WRAP OR PROTECT FOODS AND BEVERAGES, MEDICINES, CONSUMER GOODS, CHEMICALS, AGRICULTURAL GOODS, MACHINERY AND EQUIPMENT. OTHER APPLICATIONS INCLUDE THE PRODUCTION OF SPECIALISED LAMINATES FOR INDUSTRIAL AND BUILDING USES.

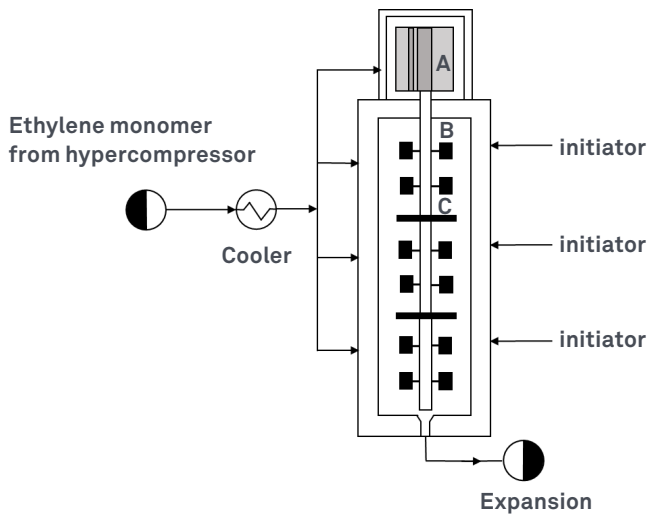
Low density polyethylene (LDPE), produced by free radical polymerization at a high reaction pressure and temperature, is the most widely used polymer grade for extrusion coating applications as it can be applied to a wide variety of substrates (1; 2). Typical substrates include paper, paperboard, metal foil, fabric or plastic film such as a biaxially oriented polypropylene, polyethylene terephthalate (PET), polyamide (PA) or cellophane. To coat the substrate, the polymer melt, which typically exits the extrusion die at a temperature between 250°C to 330°C, is deposited onto the moving substrate through a narrow flat die.

LDPE exhibits the low neck-in, low edge bead formation and high web stability that are essential for good coverage of a substrate at fast production line speeds. "Neck-in" refers to the contraction in the width of the LDPE web. Edge bead is a defect in which a larger amount of LDPE appears at the edge of the web relative to the centre. The high edge can make it difficult to feed the coated substrate into the downstream filling operation. For packaging applications, LDPE provides the high thermal stability, excellent organoleptic properties and broad sealing window which are important characteristics for ensuring the quality and integrity of any packaged products.

LDPE can be manufactured in either an autoclave reactor or a tubular reactor. The focus of this paper is to discuss the relative characteristics of extrusion coating grade LDPE made using the two processes. The particular distinctions will involve molecular weight, molecular weight distribution (MWD), degree and distribution of side short chain branches (SCB) and degree and distribution of side long chain branches (LCB).

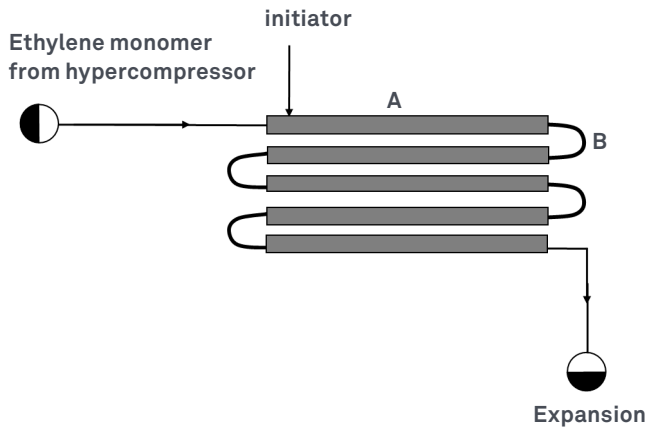
## MANUFACTURING LDPE

The free radical polymerisation of ethylene at high pressure can be performed by two manufacturing technology platforms, an autoclave reactor and a tubular reactor (3; 4). A schematic of an autoclave reactor—a continuous stirred tank reactor (CSTR)—is shown in Figure 1.



**Figure 1.** Schematic representation of an autoclave reactor: **A.** stirrer motor **B.** stirrer with proprietary design of paddles, **C.** baffle within reactor.

A schematic of the reaction section of a tubular process is shown in Figure 2. A tubular reactor can be considered as a long tube (~2000–3000m), where the reaction medium is transported as plug flow with no stirring of the reaction mixture.



**Figure 2.** Schematic representation of a tubular reactor: **A.** cooling jacket for reactor tubes, **B.** reactor tubes.

The two manufacturing technology platforms produce grades of LDPE resins with different molecular structures. Autoclave technology produces LDPE with a high degree of LCB and an increased proportion of high molecular weight molecules, creating a tree-like macromolecular structure. In contrast, LDPE macromolecules produced from the tubular process have a less extensive comb-like molecular structure (5; 6).



**THERE IS CONSENSUS AMONG RESEARCHERS AND PRACTITIONERS THAT AN AUTOCLAVE TYPE REACTOR IS INHERENTLY MORE CAPABLE OF PRODUCING LDPE WITH THE OPTIMAL PROPERTIES FOR EXTRUSION COATING.**

The broad MWD and LCB of autoclave produced LDPE is due to the wide variation in residence time of ethylene/polyethylene in the reactor, which is caused by back mixing. Back mixing occurs when the polymer/gas medium (supercritical fluid phase) meets the newly dosed cold ethylene gas. Fresh ethylene is used as a feedstock to the reactor but also to cool the reactor mixture and to keep the reaction temperature and rate under control. In addition, autoclave reactors often employ a mechanical barrier – one or more baffles that are strategically positioned within the reactor vessel. The baffles force the reactor mixture to circulate, increasing and broadening the residence time of the reactant medium. Throughout the autoclave process, inherent broad residence time distribution molecules will undergo shorter (low molecular weight) or longer (high molecular weight) growth paths. This enables autoclave reactors to produce polymers with a broad MWD and a high degree of LCB, which are desirable properties for extrusion coating operations.

In a tubular reactor, cooling takes place through the exchange of heat with the cold water that circulates around the tube. No stirrer is used for mixing. The reaction mixture travels along the reactor tube length by laminar flow so the residence time in the reactor is similar for each polymer chain. This conformity leads to the production of LDPE with a narrower MWD and less LCB than autoclave LDPE.

## CHARACTERISATION OF LDPE GRADES

Since the early days of extrusion coating, it has been widely accepted that the favourable processability of autoclave LDPE, with its stable substrate web coverage at fast line speeds, is due to its broad MWD and high degree of LCB (7-11).

Genos characterised two autoclave and two tubular LDPE resins, all with the same melt flow rate (MFR2) and the density required for extrusion coating, using gel permeation chromatography (GPC). Table 1 shows the various molecular weight measures of the resins, including the number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and higher average molecular weight ( $M_z$ ). GPC characterisation reveals that the higher average molecular weight  $M_z$  is increasingly sensitive to the presence of high molecular weight fractions in the polyethylene composition. The two autoclave process LDPE grades show a higher  $M_z$  and a broader MWD, indicating the presence of very large molecules in their composition compared to the two tubular process grades.

While GPC measurements reflect differences in  $M_n$ ,  $M_w$ ,  $M_z$  and MWD between polymers, the effect of long chain branching and MWD on measured properties are often very similar, so determining the effect of each can be quite complex. The rheology of polymer melts also reflects the molecular structure of the polymer. Rheological measurements, such as melt strength, are better suited to characterise the degree and type of LCB in a macromolecular structure.

TABLE 1. GEL PERMEATION CHROMATOGRAPHY FINGERPRINT OF LDPE EXTRUSION COATING-GRADE RESINS PRODUCED FROM AUTOCLAVE AND TUBULAR REACTOR. THE DATA WAS GENERATED AT THE GENOS TECHNICAL CENTRE IN MELBOURNE.

Process	MFR 2 190°C, g/10min	Mn g/mol x 1000	Mw g/mol x 1000	Mz g/mol x 1000	Mw/Mn (MWD)	Mz/Mn
Autoclave LDPE 1	8	25	630	4700	26	283
Autoclave LDPE 2	8	25	647	3608	26	143
Tubular LDPE 3	8	27	580	3210	21	116
Tubular LDPE 4	8	25	450	2400	18	97

Melt strength is most often determined by extruding a polymer strand through a capillary die and drawing it uniaxially through a set of accelerating nips that are located below the die. This methodology, which is known as a Rheotens melt strength test, is shown in Figure 3. The tensile force of the polymer is recorded as a function of the take-up speed of the nip rolls. Melt strength is reported as the plateau force (cN) before the strand breaks.

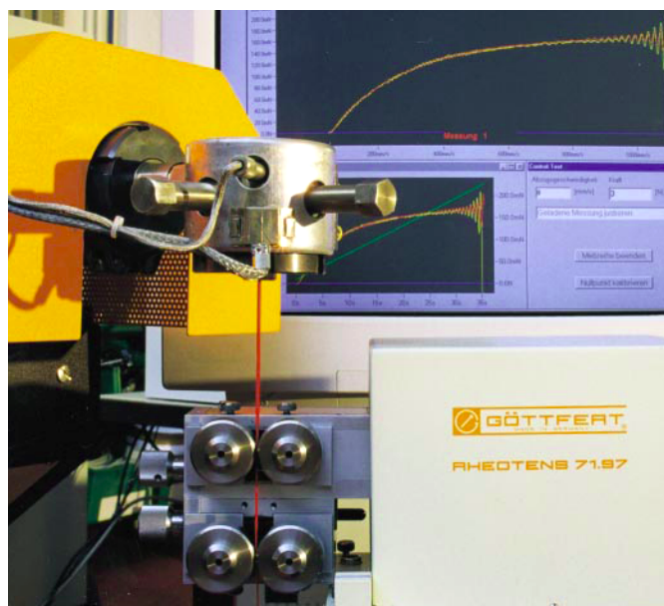


Figure 3. Rheotens melt strength test of a polymer with the raw force curve displayed on the screen (12).

Melt strength testing has become a widely accepted characterisation technique for polymers intended for extrusion coating, which is understandable given the similarity in the level of deformation that the polymer undergoes during both melt strength testing and the extrusion coating process (Figure 4). Consequently, melt strength results are often reported by resin suppliers as well as in research papers and patents (13-15).

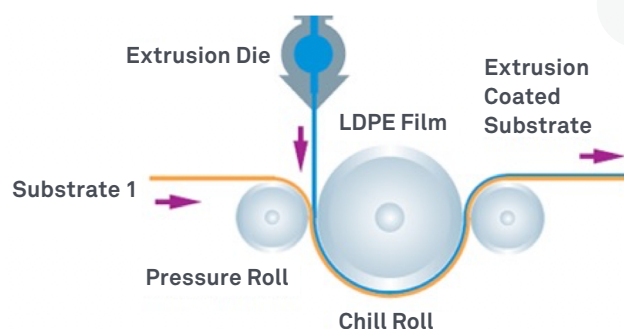


Figure 4. Extruded LDPE web being stretched in the air gap between the die and the roller by the rotational action of the chill roller.

Wagner *et al* (16) showed that the difference in the melt strength of PE relates to molecular weight distribution and branching structure. A higher degree of LCB and broader molecular weight distribution results in a greater draw down force at higher draw down ratios in the melt strength test. Bernnat *et al* (17) presented melt strength master curves for several LDPE grades produced by autoclave and tubular reactor technology (Figure 5). The results show a distinctive difference in melt strength, confirming the understanding that autoclave LDPE grades have a higher melt strength than tubular grades.

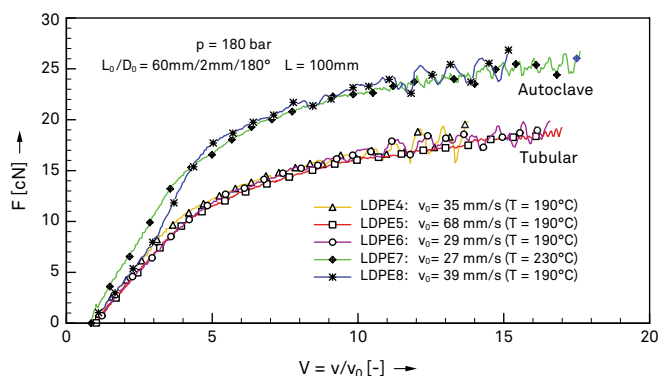


Figure 5. Rheotens melt strength master curves showing structural differences in autoclave and tubular reactor grades (17).

There is consensus among researchers and practitioners that an autoclave type reactor is inherently more capable of producing LDPE with the optimal properties for extrusion coating, including a broad molecular weight distribution, a high degree of long chain branching and high melt strength. In practical terms, autoclave LDPE offers minimal neck-in and edge-bead and has the melt strength needed for fast line speeds during the extrusion coating process.

## HOW THE RESIN MANUFACTURER CAN HELP

Genos is the leading manufacturer and supplier of LDPE extrusion coating resins to the Australian market. Genos Alkathene® LDPE is manufactured using the high pressure autoclave process, producing a range of extrusion coating resins which offer exceptional neck-in performance, higher melt strength and superior optical properties. All Alkathene® LDPE extrusion coating grades exhibit excellent organoleptic properties and outstanding heat seal characteristics.

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## Qenos Pty Ltd

471 Kororoit Creek Rd  
Altona Victoria 3018 Australia  
Phone 1800 063 573  
ABN 62 054 196 771

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