Tubular LDPE has the Extrusion Coating future.

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SUMMARY

The extrusion coating market (EC) is still dominated by autoclave LDPE. As described in the literature this is a consequence of the typical molecular mass distribution (broad + long chain branching) of the autoclave resins, which determines its processability.

Some facts:

- The average age of the European autoclaves is high (± 35 yrs).
- Autoclaves have a relatively small plant size (on average 75 ktons in Western Europe).
- Forced by European legislation, suppliers are confronted with significant license to operate investments.
- We expect that no new autoclaves will be built in the future.

At the moment no alternative polymers with comparable characteristics are available.

Security of supply of a suitable extrusion coating resin was the main driver for this project.
The performance should be at least equal to current applied autoclave resins and no hard ware modifications at the converters would be accepted.

In the market it was noticed that the next generation of EC resins will probably shift towards the molecular mass distribution of tubular resins. As we know tubular plants will continue to be built in the future. Therefore the tubular process was a logical choice.

This paper will show that after 5 years of calculating, monitoring and testing a real breakthrough is achieved in the development of an Extrusion coating grade on a tubular reactor.

1. INTRODUCTION

Approximately 50-60 years ago, the first commercial extrusion coating process started up, the plastic for coating was Low Density Poly Ethylene (LDPE). If we look to the market for extrusion coating today, we still see that it is dominated by highly branched, autoclave LDPE's. This can be explained by its unique molecular weight distribution. Autoclave LDPE is easy to process, due to its shear thinning behaviour (the viscosity decreases as shear forces increase) and due to its high degree of long chain branching (upon elongation tension stiffening takes place) good web stability can be obtained.

The total volume of PE in the extrusion coating market in Western Europe is estimated to be approximately 650 ktons. There are two clear segments defined, liquid packaging and photo-coating respectively. The definition of liquid packaging describes the companies combining the properties of plastics and other materials, especially paper, aluminium and cardboard for producing packages for food application e.g. fluid products, like non-carbonated drinks and sauces. The photo-coating segment can be described by companies combining plastic and paper for imaging applications, like Silver Halide photographic paper and ink jet paper. The rest coating segment consists of customers with different applications for extrusion coating, like release liners, medical applications, and isolation materials.

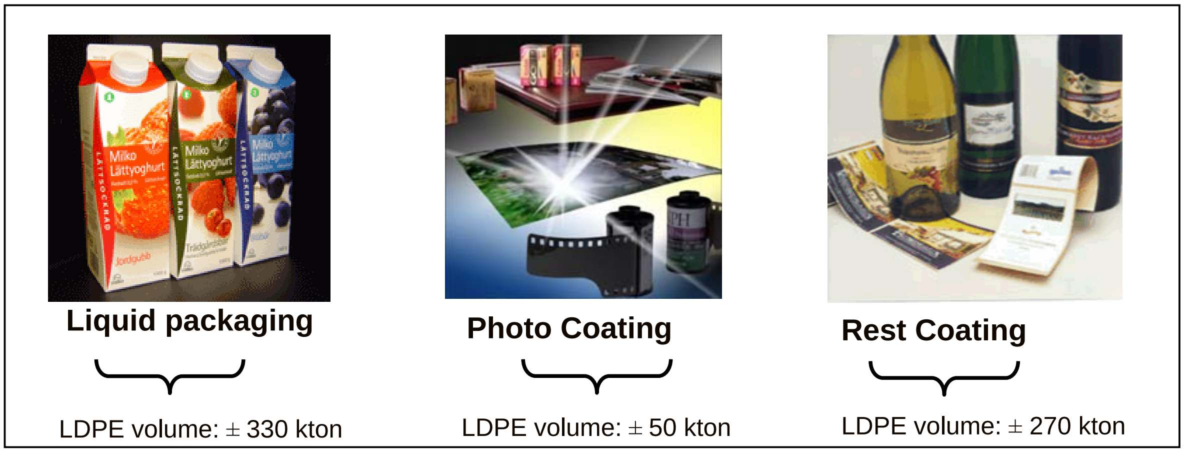


Figure 1.1: Segmentation of the Extrusion Coating market in Western Europe

When looking to the current autoclave capacity in Western Europe, this can be roughly estimated to be 2000 ktons yearly. From this capacity only 30% is really intended for extrusion coating. 20% of this volume is used for higher end-copolymers, like EVA (Ethylene Vinyl Acetate), which is often used for adhesive applications. Furthermore it can be seen that approximately 50% of the current autoclave capacity is for other LDPE market (e.g. film, injection moulding, and masterbatch). Most of these autoclaves are not able to produce the required quality; liquid packaging (high requirements concerning organolpetics) or photo-coating (extreme low gel count requirements).

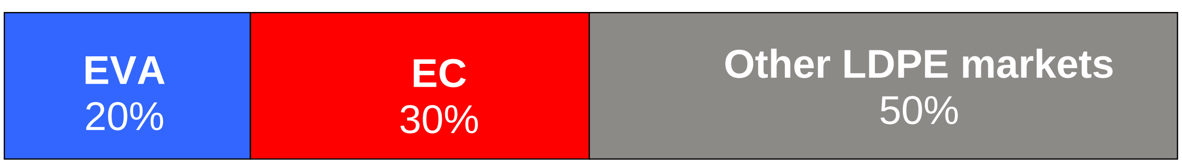


Figure 1.2: Total WE autoclave capacity ± 2000 ktons

The overall picture of the autoclaves is not very positive. The average age of these relatively small plants (~ 75 ktons in Western Europe) is approximately 35 years. Expected more severe European legislation, may force most of the current suppliers to invest significantly. Possible closures of autoclaves, heavily depends on the feedstock security (cracker integration). For obvious reasons (e.g. investment costs autoclave are 1,5 times the investment costs of a tubular plant), it is expected that no new autoclaves will be built in the future.

Based on this consideration it may be not surprising that the main driver for this project is the long term security of supply. Based on these considerations the target was to develop tubular extrusion coating LDPE as of 2001, which should be able to replace the autoclave LDPE in all extrusion coating applications. Besides this challenging goal, SABIC defined the following requirements:

- Same quality, including processability
- No hard ware modifications at converters
- No price increase

At that time it was also noticed that the processing speeds at the converters increased in time, requiring LDPE grades with less long chain branching and a narrower molecular mass distribution (MMD). This indicates that the molecular mass distribution of future autoclave materials would shift towards molecular mass distribution of tubular grades. The figure below shows an example of the molecular mass distribution difference between autoclave and tubular materials.

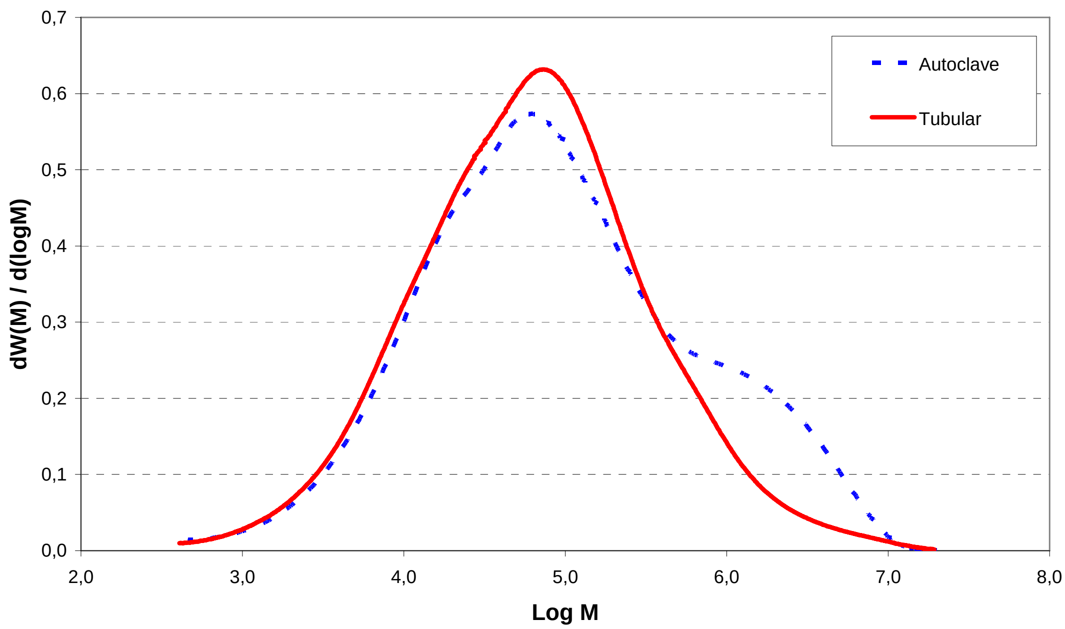
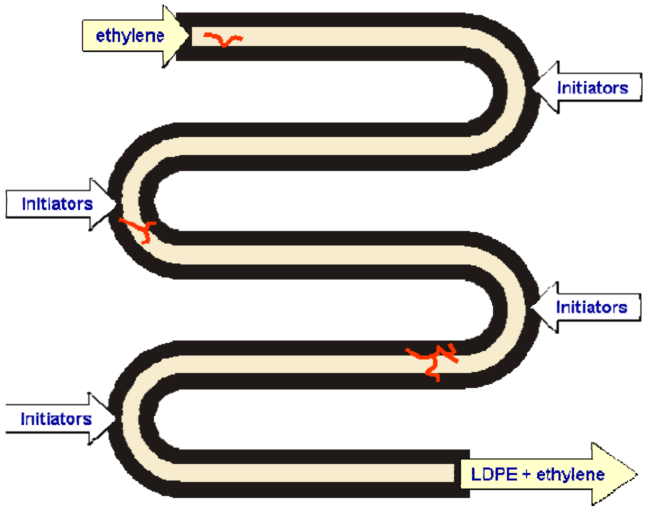


Figure 1.3: ***Molecular mass distribution measured by SEC MALLS for autoclave and tubular LDPE***

This difference in MMD can be explained by comparing the technology of a tubular reactor with an autoclave. A tubular reactor can be considered as a very long tube (~ 2000-3000m), where the mass is transported as a plug flow. Cooling takes place via the cold water that is circulating around the tube. The pressure and temperature are high and no stirrer is used for mixing, there is laminar flow behaviour at the wall. The residence time is approximately the same for each polymer chain, leading to a smaller molecular weight distribution with less long chain branching. A schematic picture of a tubular and an autoclave reactor is given in figure 1.4.
The autoclave reactor can be considered as a continuous stirred tank reactor (CSTR), cooling is performed by the ethylene that enters the reactor [1][2]. The pressures and temperatures are a little lower than for the tubular reactor. The broad molecular weight distribution in combination with long chain branching (see the high molecular shoulder of the autoclave material in figure 1.3) is obtained due to the large distribution in residence time and back mixing. Back mixing is happening when the under these conditions 1-phase polymer/gas medium (supercritical fluid phase) comes in contact with the newly dosed cold ethylene gas. According to the current knowledge, the typical MMD of the autoclave LDPE is responsible for the EC processability performance [3].



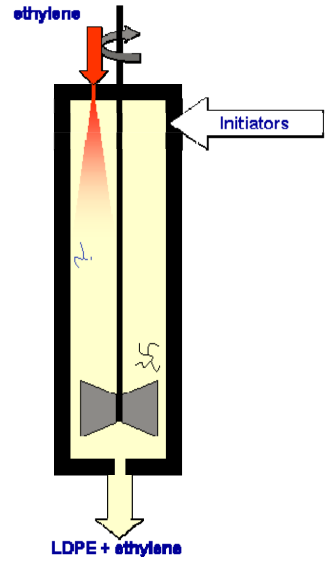


Figure 1.4: ***Schematic presentation of a tubular and autoclave reactor, respectively***

These processes are completely different, which is probably not expected considering only the grade notations [1][2].

2. EXPERIMENTAL

The experimental data related to this project were obtained from grades produced on the 3 different available tubular systems at location Geleen (The Netherlands). An overview of the different steps in the project is given below:

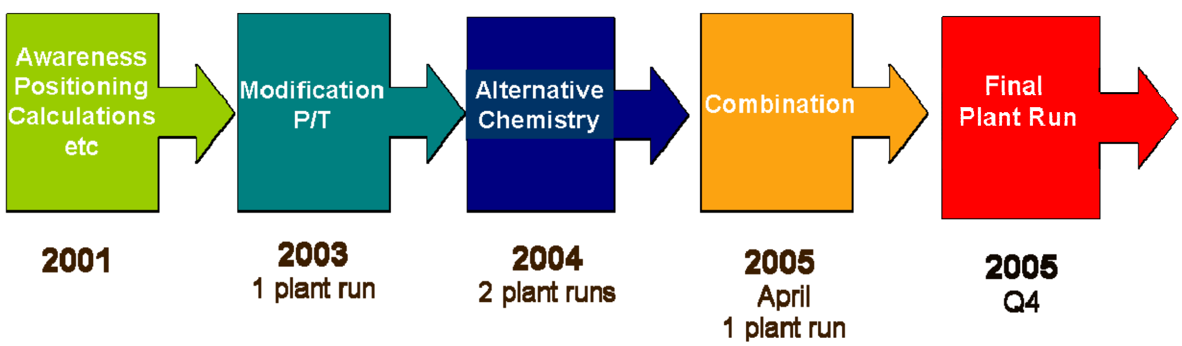


Figure 2.1 ***Different project steps for extrusion coating on the tubular***

In first stage Technical Marketing together with Research and Development put effort in preparing predictive models in order to estimate the feasibility of the project.

This stage lead to a number of production runs, which were carried out by use of an experimental design set-up [4][5]. The first three plant runs are so called proof of principles in order to estimate the impact of subsequently the production conditions and two runs focussing on alternative chemistry. As a consequence most of the runs only result in knowledge gathering instead of producing a resin with the targeted properties. Each run occupies a LDPE plant for several days and consists out of 5 up to 7 different non commercial production grades (excluding the transition materials) in the experimental set-up. Each of these production samples are extensively tested with all techniques given in paragraph 2.1.
The new tubular grade was aimed to have a density of 920 kg/m^3 and a melt flow rate of 5 g/10min. This one grade should replace the main autoclave grades used for extrusion coating.

All non-commercial grades (approximately 26 in total) were analyzed by an external laboratory. The next chapter will give a brief overview and description of the analytical techniques and the process ability tests performed on these grades. This report strongly focuses on the Extrusion Coating processability.

2.1 Analytical Techniques

An overview of the main analytical techniques as applied on all samples collected during the plant test runs is given beneath.

- Density (D_{23}) in kg/m^3 according to ISO1183.
- Melt flow rate (MFR) at 190^{o}C and 2,16 kg in g/10 min. according to ISO 1133. This measurement is performed before (on the pellets) and after processing (on the film) on the pilot EC line.
- Gel count (GC) is measured according to an internal method.
- Pentane extraction; to quantify the low molecular part present in the polymer.
- ^{1}H-NMR: on the grade and the pentane fractions at 120°C and C2D2Cl4 as solvent using the Varian Inova 600 MHz spectrometer. In order to determine the branching and unsaturation of the grades and extracts.
- SEC-MALLS (Size Exclusion Chromatography – Multi Angle Laser Light Scattering) analyses were used to determine the molecular mass distributions.
- DMS, Dynamic Mechanical Spectroscopy to obtain rheological data.
- Dynamic headspace GC is executed to determine the volatiles: ca. 30 mg sample is heated at 310°C (related to processing conditions) during 15 min.; volatiles are trapped at –150°C and subsequently characterised with on line GC (Gas Chromatography).
- Organoleptics: a panel of 10 persons made taste comparisons. Solutions were prepared from 6 grams of film per 1000 ml water. The solutions are heated for 24 hours at 60^{o}C, after which the water is filtered and a forced taste comparison is made on the undiluted test waters against filtered tasteless tap water and a reference (1808AN00). The results are evaluated by a chi-square test with paired comparison.

The tubular production trial resins (NC coded meaning non commercial grade) have been compared with SABIC LDPE 1808AN00 and 2404AN00.

2.2 Processability Properties

The extrusion coating properties are determined using our pilot extrusion coating line (PECL). The characteristics of the line are described in the brochure and on the website [6]. The processability is expressed in neck in (NI), draw down (DD) and web width variation (WV). The draw down is the maximum line speed at which the PE web breaks (ability to extend a polymer melt to a thin film). The neck in is the shrinkage in width of the LDPE web and determined at draw down speed. Web width variation is the deviation in broadness of the web during processing.

The PECL processability test is executed as follows:

- Stable processing under given conditions at 200 m/min and 10 g/m^2
- Fixation of die width and coating weight
- Exp 1: determining the draw down during constant acceleration of the line speed
- Exp.2: acceleration step wise (50 m/min); each step 5 min.; starting ≈ 150 m/min beneath the DD.

In comparison to normal production line conditions the applied test is much more severe. During this test the line speed is increased at constant extruder throughput, which results in a decreasing coating weight. Besides the temperature setting is 300 °C.
The general processing conditions of the processability tests can be found in table 2.2.1. These conditions represent more or less general processing conditions applied in the liquid packaging and photo coating market.

Table 2.2.1: Overview of some relevant PECL conditions for the processability test

Parameter	**Condition**
Air gap (cm)	30
Throttle position (mm)	10
Pressure (bar)	± 100
Die width (mm)	0.6
Die temperature (°C)	300
Coating weight (g/m^2)	10
Line speed * (m/min)	200
Substrate	Kraft paper

* Starting line speed

3. RESULTS

As mentioned previously the complete project contained several test runs, the extrusion coating performance is given below (figure 3.1).

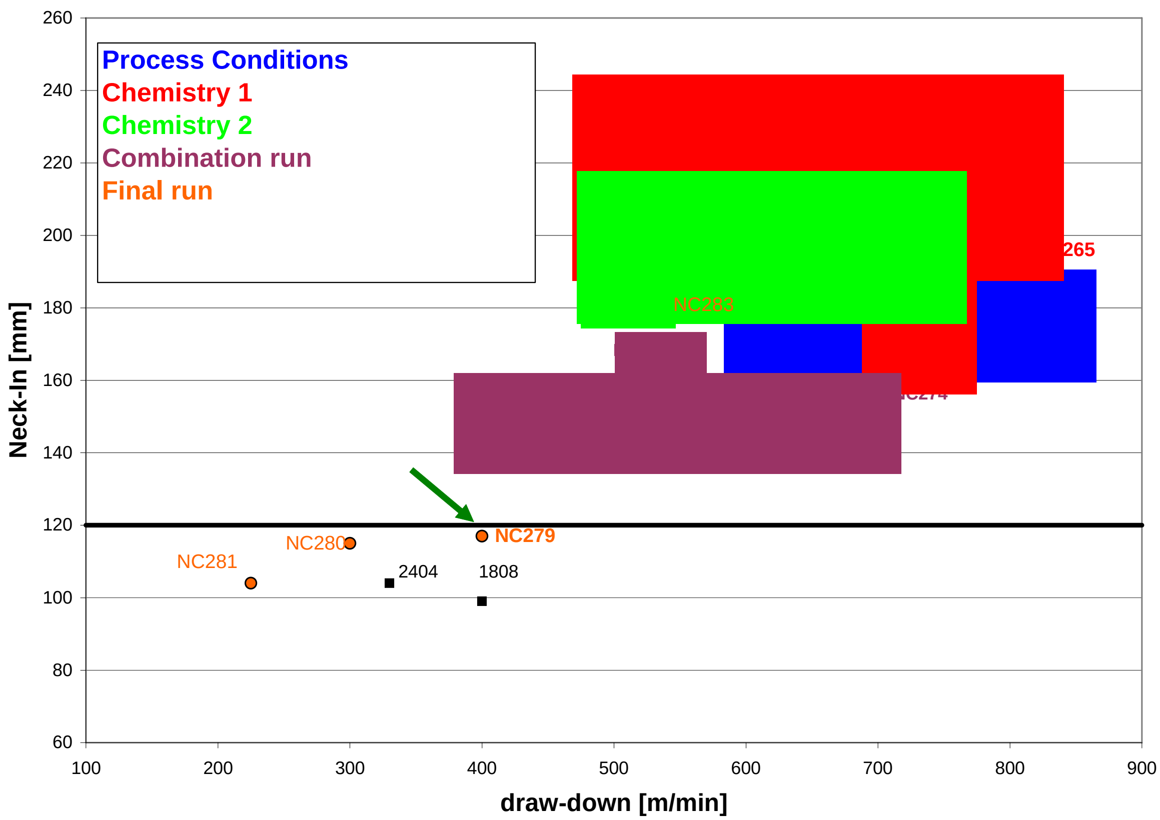


Figure 3.1 Results on DD and NI of the different project steps

During the first trial run, performed on S17, production conditions like temperature and pressure were varied in order to obtain a tubular grade with a broader molecular mass distribution. The results on neck in and draw down are given in blue in figure 3.1 (NC260, 261 and 262). The PECL processability trend of the NC materials is in the expected direction but still far from target (processability targets see table 3.2).

In the second and third plant trial runs, which were performed on S15, the focus was on the impact of alternative chemistry. The biggest achievement was the improvement of the web width variation, by using a reactive co-monomer. All tubular material so far showed a web width variation between 5 – 25 mm, which is unacceptable for extrusion coating (EC) applications. A good performance is between 1 – 3 mm. The NC266 material produced in this test run was achieving this requirement. The results on DD and NI are also given in figure 3.1 in the red cloud.

All test results of these three plant trials were mathematically evaluated in order to determine the production window of the first so called combination run.

This run included also a sample point which should meet almost all of the defined product characteristics. The NC277 was having the best performance, but still the NI was above target.
Major achievement, was that for the design of the final plant run a large production window was explored, which is also crucial for future developments. Main target of the final run was to improve the neck in without worsening the other requirements.
The final run was performed on S16, were different processing conditions could be obtained, resulting in a grade, NC279, which met all targets, including neck in.

Table 3.2 Performance of the tubular grade on the defined requirements and typicals

Product Performance Characteristics	**Analytical method**	**Unit**	**Sales Requirement (R) Typical (T)**	**NC279**
Basic properties: • Density D_{23} • MFR (190^{o}C, 2.16 kg)	 ISO 1183 ISO 1133	 Kg/m^3 g/10min	 920 ± 1.5 (R) 5 ± 0.5 (T)	 OK OK
PECL processability: • Neck in (@ line speed) • Width variation (@ line speed)		 mm mm	 ≤ 120 (R) ≤ 3 (R)	 OK OK
End properties: • Organoleptics • Gel count (600µm channel) • Food Approval Requirements Europe	 Taste panel Internal method	 - n/m^2	 No significant difference with 1808AN00 ref. resin (R) ≤ 5 (R) Equal to 2404 AN00/ 1808AN00 (R)	 OK OK OK
Stability: • MFR drop after PECL processing	 MFR_{PECL} /MFR_{start}	 -	 ≥ 5 (T)	 OK
Freedom to operate (Intellectual property rights)			Patent filed (R)	OK

The draw down value measured under very severe conditions (see chapter 2.2 processability properties) was measured to be 400m/min. At constant coating weight (10 g/m^2; which is still very low regarding most applications) a line speed of 700m/min was no problem (T_{die} = 300^{o}C). The neck in (NI) and web width variation (WV) were already constant in the range from 250 up to 700 m/min. (NI 117 mm and WV 3 mm). These processing results are well within specification and will also be suitable for customers with “lower” line speeds.

During the extensive product evaluations several potential advantages are identified. Some of these will be mentioned.
The tubular grade is very stable, a very small melt index drop after processing is observed. Consequently the product is less machinery dependent and has an improved consistency in end properties. Figure 3.3 shows a

comparison between the tubular grades and the most common autoclave grades for extrusion coating 2404AN00 (MFR: 4.2 g/10min), 1808AN00 (MFR: 7.5 g/10min) and 1815AN00 (MFR: 15 g/10min).

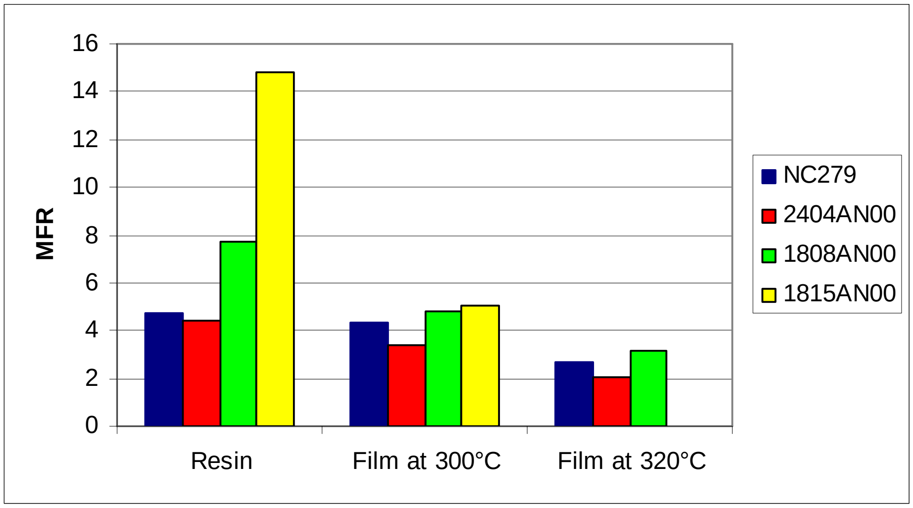


Figure 3.3: ***MFR of NC279, 1808AN00, 2404AN00 and 1815AN00 at different processing conditions.***

As can be seen from this figure the melt flow rate decreases with higher processing temperature. After processing at 300°C the 1815AN00 encounters the largest melt index drop, but the melt flow rates of all films are very close, namely between 4.4 and 5 g/10min.
This is a strong indication that the rheological/flow behaviour after processing is comparable in spite of different starting melt flow rates.

Furthermore, during extensive PECL processing it was found that the NC279 was able to be processed at high line speeds with lower temperatures. During this test the coating weight was kept constant at 10 g/m^2, the test was stopped at 800 m/min. As can be seen from figure 3.4 the NC279 has reached the maximum line speed of 800 m/min already at 290°C, while the 2404AN00 and the 1808AN00 need a temperature of approximately 310°C in order to obtain this line speed.

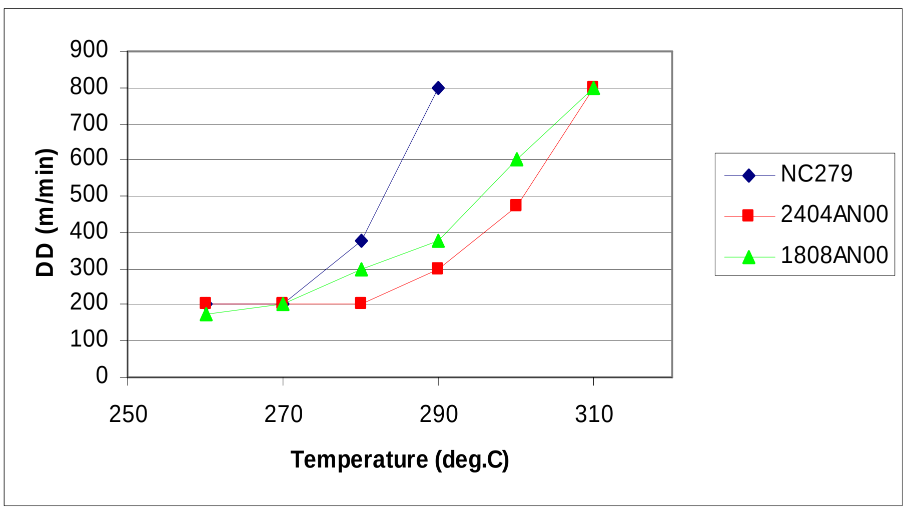


Figure 3.4: ***DD against temperature for NC279, 2404AN00 and 1808AN00 at constant coating weight of 10 g/m^2***

Often in extrusion coating, high extruder temperatures are necessary in order to obtain good adhesion between the paper and the PE. The NC279 gives very good adhesion, which was expected taking the chemical structure of the applied co-monomer into account.

Important to notice is that, when the extruder temperature can be lowered there are specific advantages during processing such as:

- Less uncontrolled chemistry in the extruder; less product degradation during processing (less MFR drop)
- Improved organoleptics
- Less deposit in the extruder, sieves and die.

In case line speed optimization at the customer production line is restricted due to adhesion limitations, the tubular grade potentially enlarges the possibilities to increase the line speed with sufficient adhesion.

The motor load of the tubular grade is lower in comparison to autoclave LDPE's (see figure 3.5). This makes it possible to apply the earlier mentioned lower processing temperature, without exceeding the motor load of the autoclave LDPE at elevated temperatures.

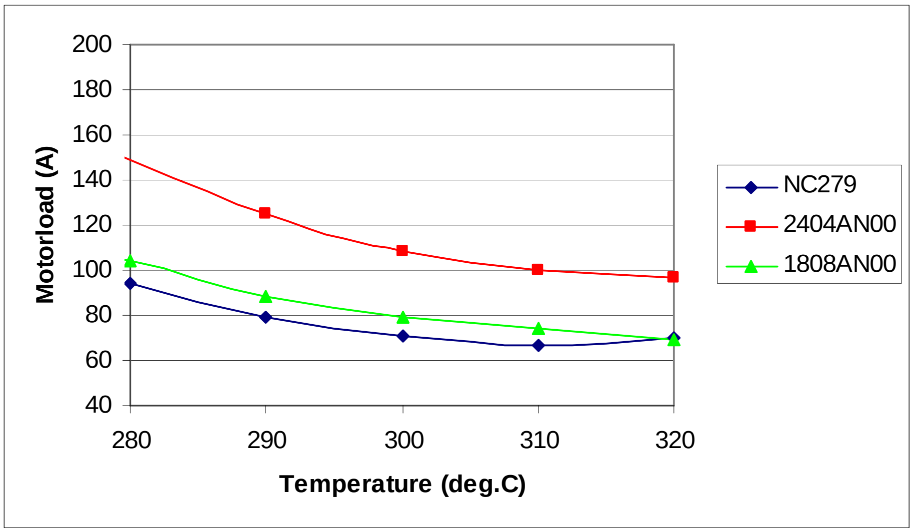


Figure 3.5: ***Motor load at different temperatures for NC279, 2404AN00 and 1808AN00 at constant coating weight of 10 g/m²***

These possible product advantages require further investigations.

4. CONCLUSION & FOLLOW UP

After 5 years of calculating, monitoring and testing a real breakthrough is achieved in the development of an Extrusion coating grade on a tubular reactor. With this invention SABIC secured the long term of supply for the extrusion coating market. The final developed product fulfills all targeted requirements and even some possible improvements are expected.

This production technology is generally applicable to all tubular techniques. Some major hardware changes are necessary in order to produce an extrusion coating LDPE with tubular technology.
In order to prepare for the market introduction in 2008, the plant modifications will take place at the Geleen site in 2007.

5. ACKNOWLEDGEMENT

The authors would like to thank all project members and the extrusion coating line operators for their valuable contribution to the project.

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