NEW ACRYLATE BASED RESINS FOR EXTRUSION COATING

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Abstract
DuPont has started to market new adhesive, sealant and peelable resins formulated around ethylene-acrylate copolymers produced on tubular reactors. This type of reactors and their operating conditions can produce copolymers with properties significantly different from the properties of copolymers produced on conventional autoclave reactors. This paper will describe some properties and outline new applications in extrusion coating.

1. Introduction

Ethylene alkyl acrylate copolymers have been produced for years by several different manufacturers in Europe and overseas. Two years ago, DuPont started to market ethylene alkyl acrylate copolymers of low-density polyethylene produced by Special Polymers Antwerp (SPA), a 50/50 joint venture with Borealis, on two tubular reactors with a total capacity of 120'000 tons/year. This plant produces now ethylene butyl acrylates (EBA), ethylene ethyl acrylates (EEA) and ethylene methyl acrylates (EMA). The present paper will concentrate on new applications in food flexible packaging of resins formulated around EMA only. New applications of EMA in other fields and applications of EEA and EBA will be communicated later.

2. Properties of ethylene methyl acrylate produced on tubular reactor

The alkyl acrylate copolymers exhibit a high degree of thermal stability and therefore process very well on extrusion coating lines. We quantify the degree of thermal stability in extrusion coating by a special test called "Melt Index Stability". In this test, the pellets are submitted to a temperature of 290C - a typical melt temperature in extrusion coating – for thirty minutes in the melt indexer. The melt indexer is then cooled down to 190C and we measure the weight of polymer going out under a weight of 2.16 Kg during ten minutes. The melt index stability is defined as the ratio of the MI after thermal treatment divided by the MI without such a treatment. Thermally stable resins will give MIS close to one. The table 1 below compares MIS of different ethylene copolymers currently used in extrusion coating.

Table1: Melt Index Stability of ethylene copolymers

Surlyn® 1652	E/8%MAA	E/6%AA	E/13%MA	E/20%MA
0.6	0.5	0.4	1.0	1.3

The MI of ethylene methyl acrylate with 20%MA slightly increases whereas the MI of ethylene methacrylic acid (EMAA) or ethylene acrylic acid (EAA) copolymers decrease under thermal treatment. As the viscosity of EMAs decrease with temperature and with time, these polymers can easy be purged out of extruders.

New types of ethylene alkyl methyl acrylate with improved adhesion to polyester and polypropylene films were presented at the 1997 Tappi Conference (Ref.1) and are patented (Ref.2 and Ref.3) by Chevron. These resins are produced on a high-pressure autoclave reactor characterized by four distinguished zones connected in cascade. This allows to control the ratio of ethylene to alkyl in each zone.
The reaction conditions on the SPA tubular reactors can be adjusted to control the distribution of the methyl acrylate groups along the ethylene backbone. We can produce EMAs with a higher melting temperature versus the one of random copolymers produced on conventional high-pressure autoclaves. Figure 1 gives the melting temperatures of EMAs produced on tubular and autoclave reactors measured by DSC according to ASTM D-3418. For an EMA with 20%MA by weight for instance, the melting temperature is 20C higher when produced on a tubular reactor.

3. New adhesive to PET and PVDC

Bynel® 22E757 is a co-extrudable adhesive developed for extrusion coating or extrusion lamination with bi-axially oriented polyester films without primers. It has been formulated around an EMA produced on the SPA tubular reactor.

To evaluate adhesion, a 3 layers sample was prepared on our pilot line. Mylar®23A, a 23 microns bi-axially oriented polyester film available from DuPont Teijin Films, was corona treated on-line prior coating at 4,5 kW over its width of 0,55 m. We co-extruded coated at 100 m/min line speed with a 10 microns layer of BY 22E757 in contact with the polyester film and a 10 microns layer of a low-density polyethylene (LDPE with 4MI, 924 Kg/m3) with a melt temperature of 320C for both resins. BY 22E757 was introduced in an extruder having 2,5 inch in diameter and the polyethylene in an extruder having 3,5 inch in diameter. Both extruders had a length over diameter ratio of 30. The die-gap was set at 0,7 mm and the air-gap was set at 0,15 m.

The T-peel strength of BY 22E757 to the oriented polyester film was determined using the internal test method T93 (100 mm/min pull speed, 90 degree). We could not separate the coated layer from the film (tensile strength smaller than T-peel strength).

We further studied the influence of melt temperature. The same BY 22E757 was co-extruded with the same LDPE on bi-axially oriented PET-film. The co-extruded layer thickness were 10 and 40 microns respectively for the BY 22E757 and LDPE. The thickness of the LDPE layer was increased in order to avoid breakage during measurement of the T-peel strength that are reported in the table 2.

Table 2: Effect of melt temperature

Melt temperature (C)	T-peel strength (N/15mm)
320	4.9
310	4.5
300	4.1
290	3.8

For a melt temperature set at 320C, for a line speed at 100 m/min and for layer thickness of 10 microns for BY 22E757 and 40 microns for LDPE, the T-peel strengths with and without corona treatment of the polyester film are given table 3.

Table 3: Effect of Corona

Treatment	T-peel strength (N/15mm)
With Corona	4.9
Without Corona	1.4

The influence of line speed is given below on table 4 for a melt temperature of 320C, 0.15 m air-gap and a corona treatment of 4,5 kW over 0,55 m.

Table 4: Effect of line speed

Line speed (m/min)	T-peel strength (N/15mm)
100	4.9
150	3.9

The thinner sample boPET//BY 22E757/LDPE, 12//10/10 microns that could not be separated was dipped in water during a period of 6 weeks The adhesion was 3.6 N/15mm after this treatment.

We have also investigated the adhesion of a co-extruded laminated structure boPET//BY 22E757/Nucrel®3990//Al with layer thickness of 12//4/8//7 microns respectively. The structure was manufactured on a production line at 200 m/min, 320C melt temperatures with Corona treatment on the polyester film.

The samples were dipped in water and in olive oil. After 3 months at room temperature, we could not separate BY22E757 from the boPET-film.

We evaluated adhesion to PVDC coated on paper and found good bond, provided the substrate is Corona treated on-line before coating. On the sample paper//PVDC//BY 22E757/Ionomer 1652 with the co-extruded layer thickness of 10/20 micron we measured 4N/15mm as T-peel strength. The line speed was 100 m/min and the melt temperatures 310C.

The same BY 22E757 has found applications in the cast sheet process as an adhesive between the co-extruded PET and LDPE. On the cast film PET/BY 22E757/HDPE, 25/12/75 micron produced in our laboratory, we measured 12N/15mm as T-peel strength between BY 22E757 and PET (Selar®PT 8307).

4. New Seal/peel resin

DuPont started to market seal/peel resins about 15 years ago. The EMA based grade 1184 was the first grade introduced for extrusion coating with seal/peelability to both Polystyrene and Polypropylene. The EVA based grade 11D554 has then been introduced for its lower seal initiation temperature, good hot-tack and excellent organoleptic properties. Now the new grade Appeel® 20D745 formulated around EMA from SPA gives the highest seal/peel resin to APET as it can be seen on Figure 2. The seal/peel strength was measured following DuPont internal method T94 (1 s sealing time, 0.3 MPa sealing pressure, 100 mm/min pull speed at 180 degree) on samples Al//Acid-copolymer/Peel-resin produced on our pilot line with layer thickness of respectively 40//10/10 microns.

The universal seal/peel resin AP 20D745 is peelable to a large number of materials as one can see on Figure 3 (WR03-1). The seal/peel strength to PET, PP, PS and HDPE is between 6 and 10 N/15mm over a wide range of temperatures (160 to 220C).

AP 20D745 can be extruded at melt temperatures as low as 240C if taste and odor is an issue and if adhesion to the substrate is good enough as for instance when co-extruded with an acid copolymer on Al-foil. It can also be extruded at temperatures as high as 320C for instance if activation of a primer is needed. We suggest 2% of the additive Conpol®20S2 to reduce sticking to the chill-roll and to lower the COF at the same time.

The new grade AP 20D745 gave also good seal/peel values to PET based lacquers used sometimes to protect Al trays against corrosion.

The aluminum based peel lid structure can easily be embossed, precut and stapled to feed the filling/sealing machines for applications in the diary industries.

Different other substrates can be considered for coating on. Paper//PA6/BY 4288/AP 20D745 is another commercial application for roll fed lids with thin paper or precut lids with thicker paper or board.

Extrusion coating on PET sheet is under development. We faced zipping (fluctuations in seal/peel strength) which causes noise when opening. The zipping was not observed with neither aluminum based peel lids nor paper based peel lids. We believe it is due to the rigid polyester sheet. This induces a low peel angle which is known to give this phenomena. We could overcome the zipping problem by a new formulation.

The grade AP 20D745 complies with the European and US regulations for direct food contact.

The total migration (10 days at 40C) has been measured on the sample Al//NU 3990E/98%AP 20D745+2%CO 20S2, 30//10/10 microns: 4 mg/dm2 in olive oil, 1.9 mg/dm2 in acetic acid (3%) and 0.9 mg/dm2 in ethanol (10%vol), this means below the authorized value of 10 mg/dm2.

5. Conclusion

Ethylene Methyl Acrylates are very easily processed in extrusion coating because of their melt index stability close to 1 at melt temperature of 290C.

Ethylene Methyl Acrylates produced on tubular reactors have higher polarity. This allowed to develop new adhesives specially on PET in cold and warm state and PVC. They give an opportunity to innovate in the market of flexible packaging structures.

EMA, EBA and EEA copolymers complete DuPont's offering in ethylene copolymers as ionomers, acid copolymers and EVA.

References:

1 Coatings & Laminates of improved ethylene alkyl acrylate copolymer with polypropylene and polyester, Richard Schmidt, Tappi Polymers, Laminations & Coatings Conference, 1987, p. 397/400

2 U.S. Patent 5'532'066 titled "Laminate of Ethylene-Alkyl Acrylate Copolymer and Polyester", Latiolais et al., July 2nd/1996

3 U.S. Patent 5'543'233 titled "Laminate of Ethylene-Alkyl Acrylate Copolymer and Polypropylene", Latiolais et al., August 6th/1996.

Fig.1 EMAs from Tubular vs Autoclave Reactors

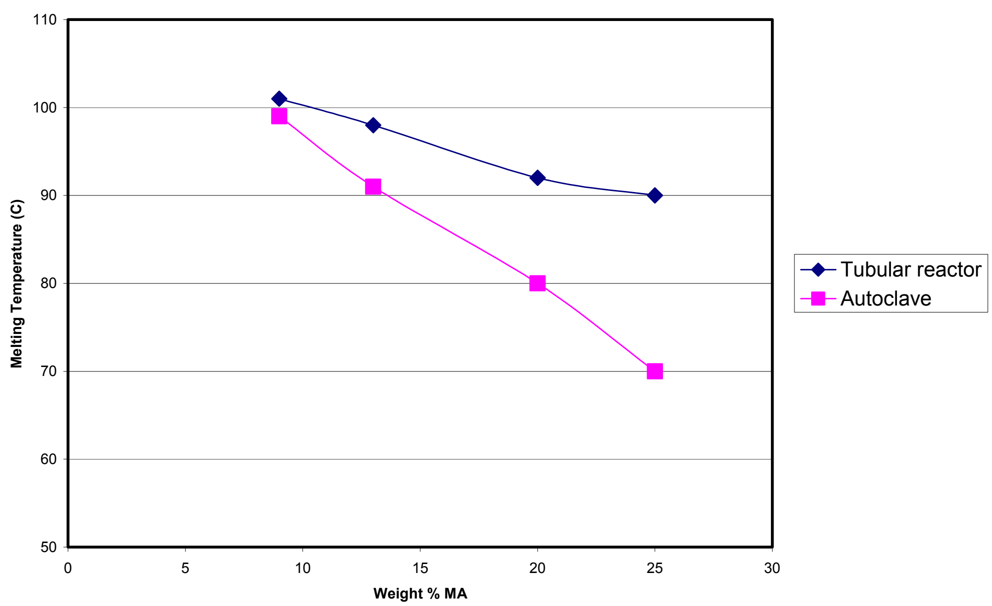


Fig. 2 Seal/Peel to APET

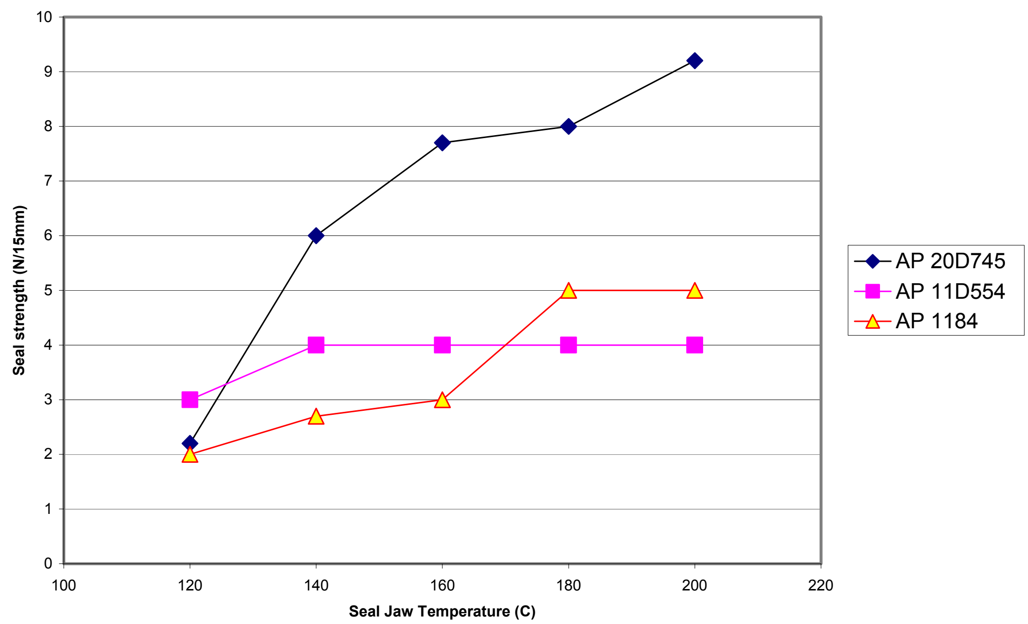
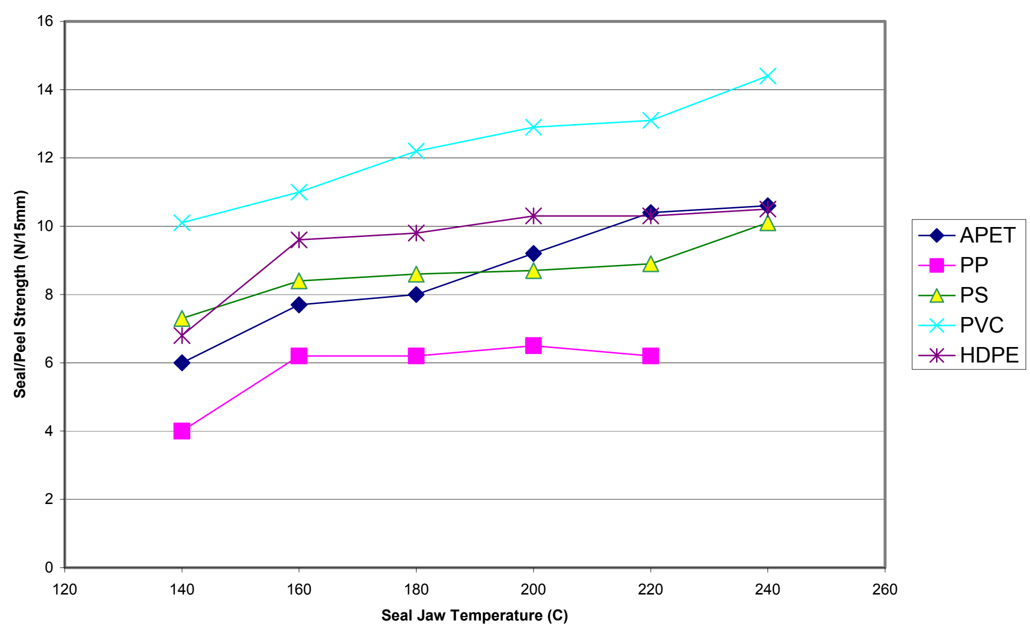


Fig. 3 Seal/Peel Strength of AP 20D745 to different substrates



The miracles of science

New acrylate based resins for extrusion coating

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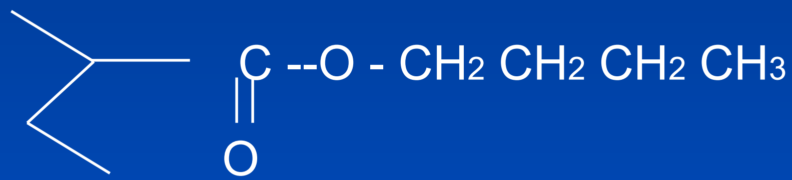
Tappi,
Rome, May 12th-14th/2003

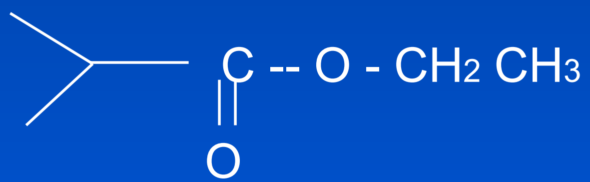
Specialty Polymers Antwerp

Molecular structures of Ethylene Alkyl Acrylates Copolymers

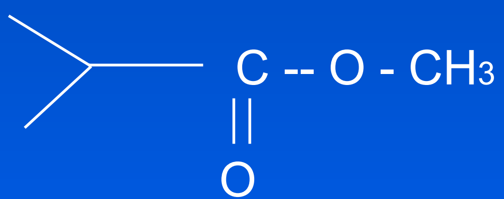
EBA



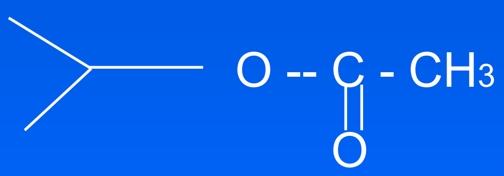
EEA



EMA



EVA

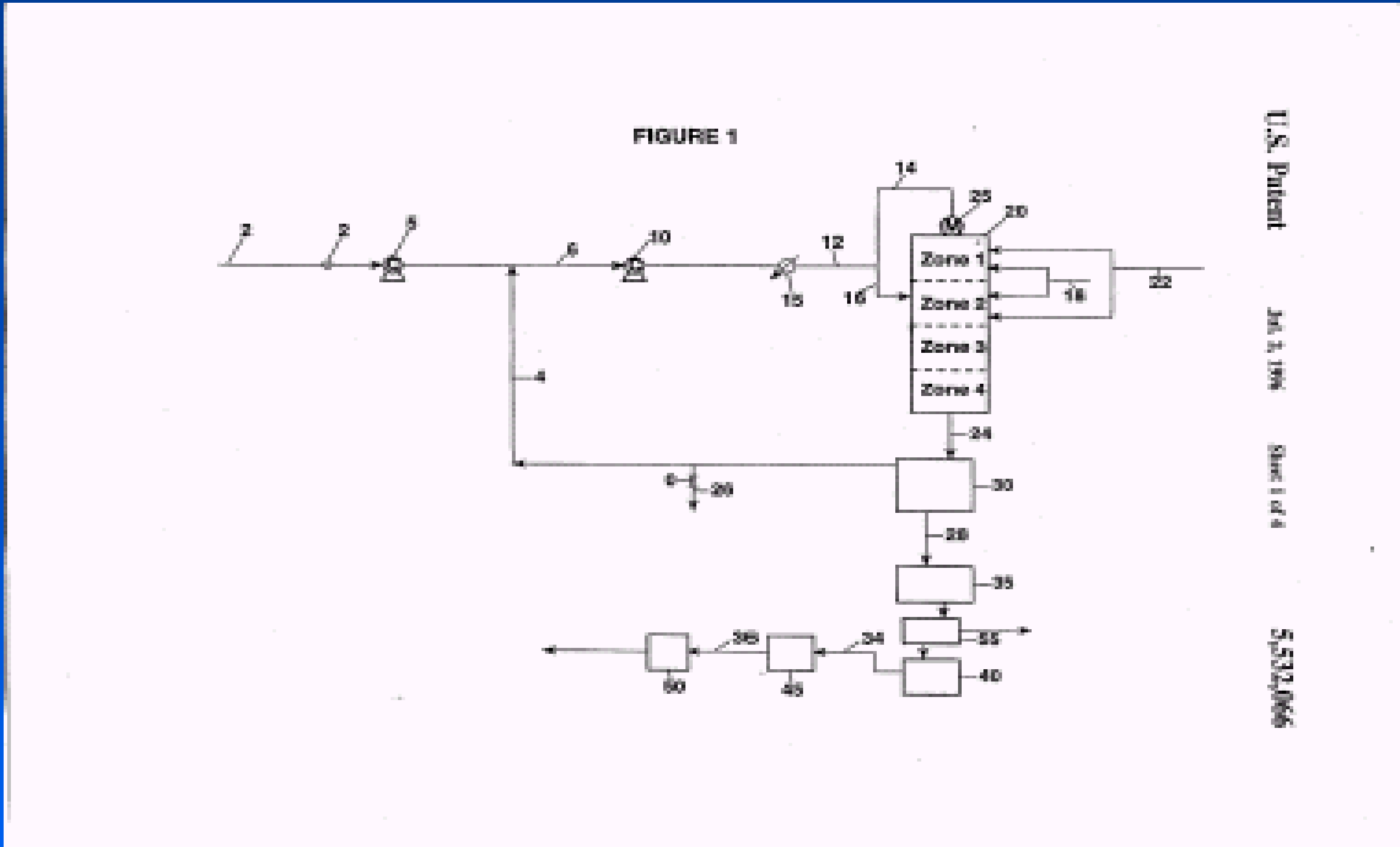


Melt Index Stability (MIS) of ethylene copolymers

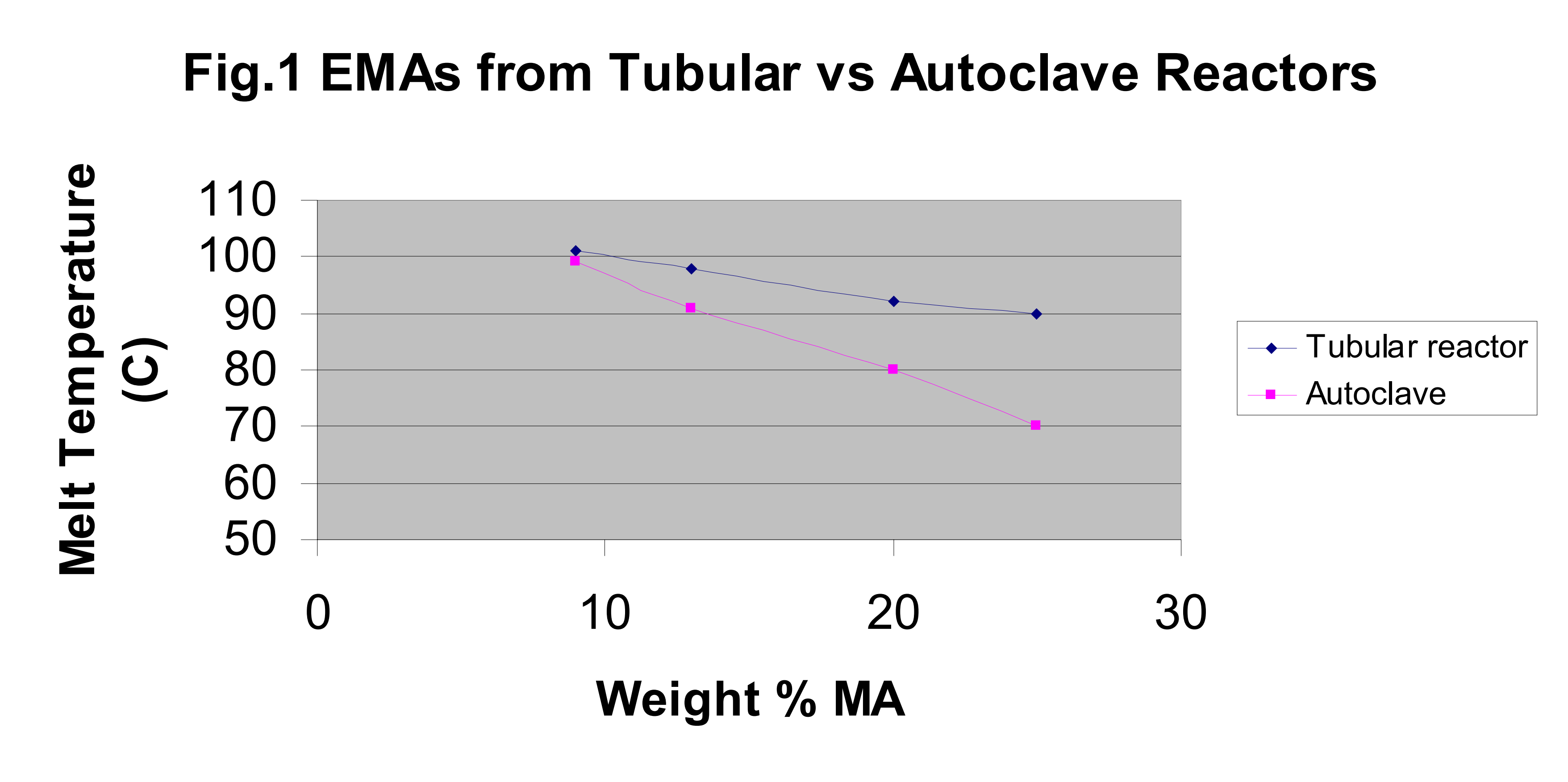
MIS = MI after 290C, 30min / MI

Surlyn® 1652	0.6
E/8%MAA	0.5
E/6%AA	0.4
E/13%MA	1.0
E/20%MA	1.3

New Acrylate Process (Chevron)



EMA from tubular reactors: higher melting temperature



Co-extrudable adhesive to boPET

Mylar®23A//**Bynel®22E757**/LDPE(7MI), 23//10/10 μm
Could Not Separate
(Tensile strength of coating < T-peel strength)

Processing parameters:
320ºC melt temperature
Corona treatment in-line of plain Mylar® (4.5 kW/0.55m)
100 m/min line speed
0.7 mm die gap
15 cm air-gap (90 ms TIAG)
30 kN/m force on the nip

Effect of melt temperature

boPET//**BY 22E757**/LDPE(7MI), 23//10/40* µm
*Thicker coating to enable adhesion measurement
Corona, 100 m/min.

Melt Temperature ºC	Adhesion N/15mm
290	3.8
300	4.1
310	4.5
320	4.9

Effect of Corona

boPET//**BY 22E757**/LDPE(7MI), 23//10/40 μm
320C, 100 m/min, 15 cm Air-gap.

With Corona: 4.9 N/15mm
Without Corona: 1.4 N/15mm

Effect of line speed:

boPET//**BY 22E757**/LDPE(7MI), 23//10/40 µm
320°C, 15 cm Air-gap, Corona.

100 m/min (90 ms TIAG): 4.9 N/15mm
150 m/min (60 ms TIAG): 3.9 N/15mm

Aging in water and oil

BoPET//**BY 22E757**/LDPE(7MI), 23//10/10 μm
Pilot line, 320°C, Corona, 100 m/min.
1 week aging in air: CNS
6 weeks immersed in water: 3.6 N/15mm

boPET//BY 22E757/Nucrel3990E//Al, 12//4/8//7 μm
Production line, 320°C, Corona, 200 m/min
3 months in olive oil: CNS

Co-extrudable adhesive to PVDC

Paper/PVDC//**BY 22E757**/Ionomer 1652

10 µm 20 µm

Pilot line, 310 ºC, Corona, 100 m/min

T-peel strength: 4 N/15mm

Co-extrudable adhesive PET/PE

Cast Film:
PET/**BY 22E757**/HDPE, 25/12/75 µm

T-Peel strength: 12 N/15mm

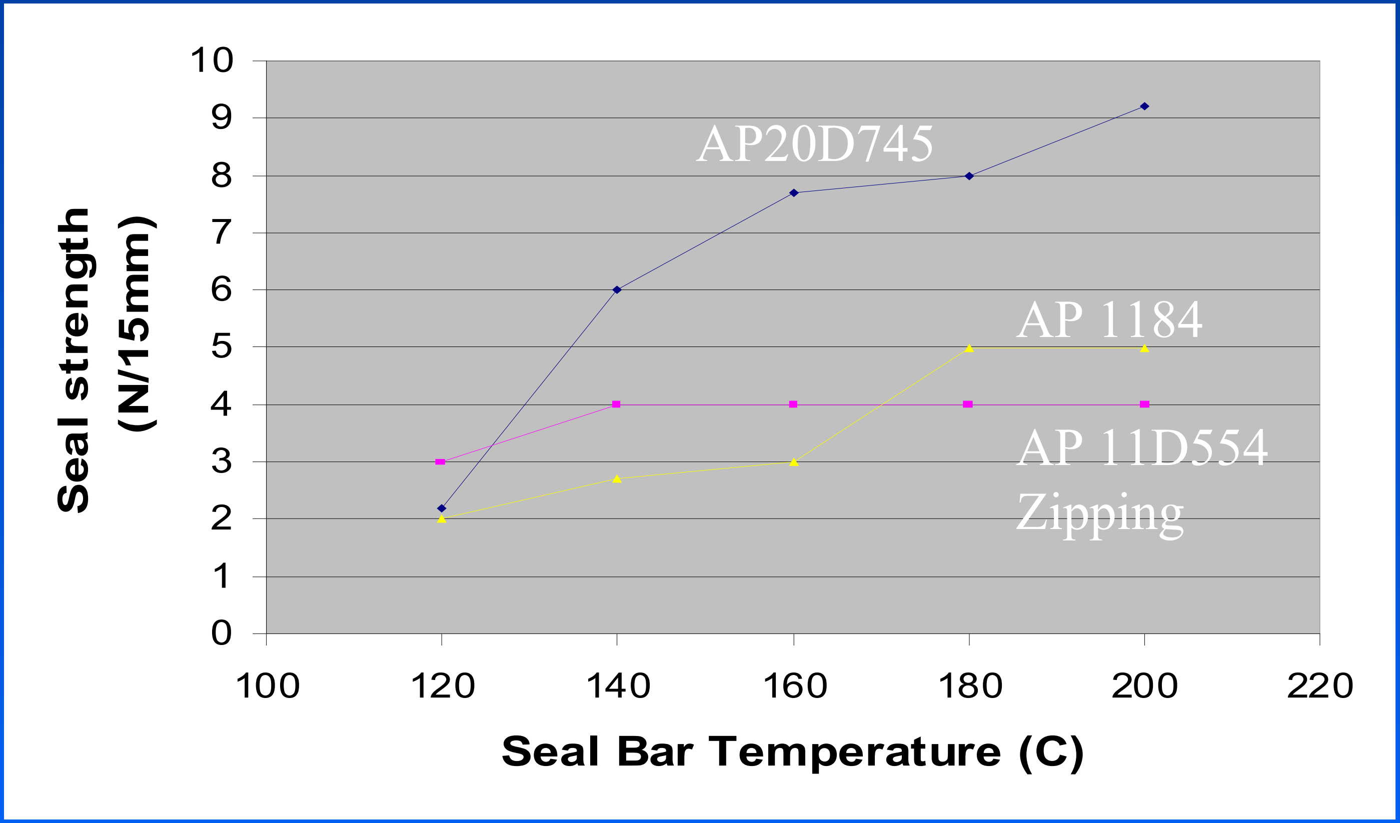
Adhesion to other substrates

Co-extrusion **BY 22E757**/LDPE(7MI), 23//10/10 µm
320°C, Corona, 100 m/min.

oPET: CNS (excellent)
oPP: 2.5 N/15mm (fair)
oPA: 0.4 N/15mm (poor)
paper: fiber tear (excellent)
Al: poor (similar to PE)

Appeel® 20D745
highest seal/peel strength to APET

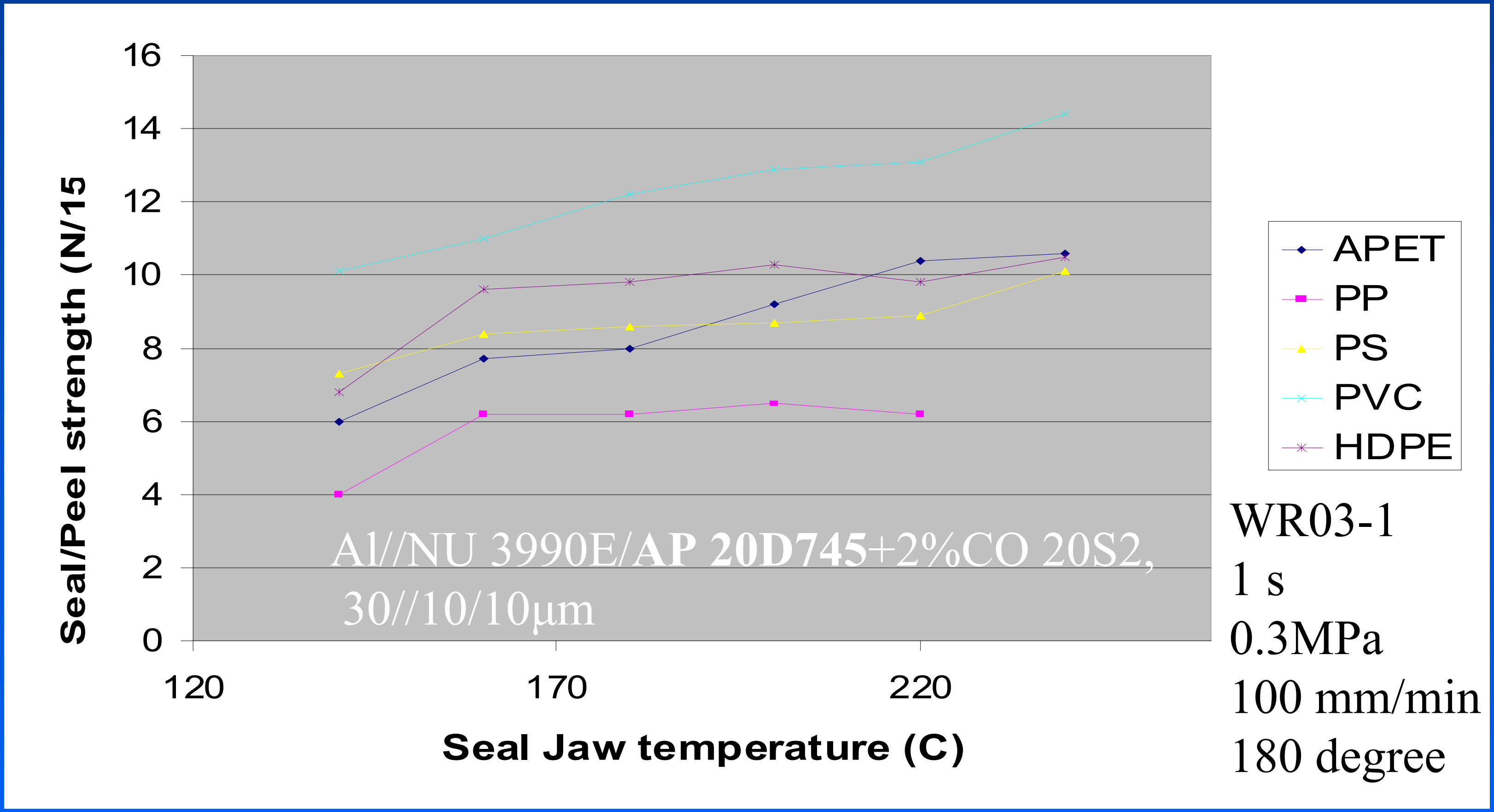
Al//Nucrel® 3990E/AP, 40//10/10 µm



WR950838
1 s
0.3 MPa
100 mm/min
180 degree

Universal AP 20D745

Seal/Peel strength to APET, PP, PS, PVC, HDPE



Structures of peel lids

Al//NU 3990E/**AP 20D745**, 30//6/12 µm

Paper//PA6/BY 4288/**AP 20D745**, 50//15/5/10 µm

PET//BY 22E757/**AP 20D745**, 50//5/10 µm

, 200//10/20 µm

Conclusions

EMAs are easy to process in extrusion coating with MIS of about 1

EMAs produced on tubular reactor give high adhesion to PET and PVDC

Large offering of ethylene copolymers: ionomers, acid copolymers (EMAA and EAA) EVA and now EMA, EBA and EEA.