Radiation Chemistry and Modification of Polymers

(Part 2)

Advanced Applications

Staff Training

Outline

March 4, 2008

- Radiation Chemistry of Polymers
- Radiation Modification of Polymer Formed Parts 成型部件
- Radiation Modification of Bulk Polymer Resins 高分子树脂

March 5, 2008

- Radiation Processing Basics
- Radiation Stability of Polymers in Sterilization

Cross-linking of Engineering Plastics

Main interest:

- PET (polyethylene terephthalate)
- PBT (polybutylene terephthalate)
- Nylon (polyamide)

Commercially available: Frianyl® (Nylon) from Frisetta; Vestodur-CL® (PBT) from Degussa; Creamid® (Nylon) from PTS

Needs: Lead-Free Soldering 无铅焊接 Requirements

- Soldering heat resistance: 260ºC x 60 sec. for electric and electronic applications.
- Other requirements
  - Flame resistance: UL94 V-0
  - Injection stability: viscosity stays at 10-100 Pa•s after 60 min.
  - UL temperature index: >100 ºC
  - Water absorption for Nylon: ≤1.2%
  - Even higher temperatures: 350ºC x 3 sec. and 450ºC x 1 sec.

Solution: Radiation Crosslinking

- To enhance the heat resistance and thus avoid using more expensive high performance polymers (e.g., PPS, PEEK, LCP).
- A radiation cross-linking promoter ("pro-rad", "sensitizer") is melt-blended (by extrusion compounding) with the engineering plastics.
- The blend is injection molded or extruded into part, and the part is irradiated by EB, gamma or X-ray. Radiation dose can be 60 to 400 kGy.

Radiation Cross-linking Promoters

Multifunctional monomers or polymers

- Triallyl cyanurate (TAC) and triallyl isocyanurate (TAIC)
- Acrylates and methacrylates (e.g., glycidyl methacrylate, TMPTMA)
- 2-6 wt% of polymer
- Melt blending (extrusion compounding) is crucial
- Acetylene-impregnation of PBT or PET was also reported

Other Components in the Formulation

- Antioxidant
- Stabilizer
- Flame retardant
- Other application-specific additives

Schneider China:
PTS Nylon Crosslinking

Gel content issue

Solvent extraction:

Gel % = w_1/w_0

w_1 – before extraction

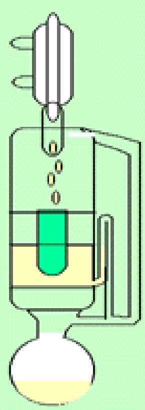
w_0 – after extraction

Soxhlet extraction

An alternate approach to extracting solids.

Repeated soaking of the solid prevents formation of channels

Rapid return of cool fluid can represent a hazard. Solvent should not be flammable.



PTS-MARKETING **TECHNICAL INFORMATION**

V-PTS-CREAMID-A3H2G5 * M0311A/13 blau 09.12.2002

PA6.6 25%GF+HS/UL94/E-17399

V-PTS-CREAMID-A3H2G5*M0311/13 is a cross-linkable PA6.6 with 25 % glass fibre (pellet mix).

This material contains a special package of BETALINK (cross-linking agent) and antioxidants which is developed for cross-linking by
e-beam radiation and electro-technical applications.

With a radiation dose of 100 kGy (beta) moulded parts can be cross-linked.

The chemical resistance is significantly improved.
The gel value in formic acid after cross-linking is typically about 77 %.

Cross-linked parts are passing without flame retardant additives the glow wire test (960°C) according to IEC 695-2-1 at 1.6 mm wall-
thickness.

After cross-linking the parts pass the penetration test with the PTS cross-linking tester at 350°C (2mm diameter, 1 kg load) without penetration.

Typical applications

- relais carriers
- connectors and elements for SMD soldering technique (280°C)
- coils for high temperature soldering techniques (400°C/3 sec.)
- housings for power switches

Properties according to UL card:

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Flame class = HB      HWI 0,75 mm = 0       HAI 0,75 mm = 0
RTI (elec.) = 150°C     CTI = 0     (see UL file no. E 173999)
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Processing conditions:

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Melt temperature    :  258°C
Moulding temperature:  265-290°C
                    Hopper                                  Die
Temperatureprofile: V-------------------------------------->
                    280 / 290 / 285 / 280 / 275 /°C +-10°

Mould temperature   :  70-120°C
Pre-drying          :  The material is packed in multi-layer bags
                       with Aluminium film and can be used without
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The information presented herein is true and accurate to the best of our knowledge, but without any guarantee.

Radiation Cross-linking of Nylon

Property	Nylon66	Crosslinked Nylon66* (60 kGy)
Tensile Storage Modulus @ 260°C (MPa)	0	30
Water Absorption (%) (23°C x 24 hrs)	1.2	1.2
UL Temp. Index (°C)	ND	104
UL94 V-0 (with bromine FR)	pass	pass

* With TAIC (trially isocyanurate) as cross-linking promoter 交联促进剂

Reference: S. Okabe et al., "Development of radiation Crosslinking Nylon Molding Compound", *SEI Technical Review*, 59, 48-51, 2005

Property Enhancements from Irradiation: PBT and Nylon

Resin	Crosslinked PBT	Crosslinked Nylon66
Radiation Dose (kGy)	100	100
260^{o}C x 60 sec. soldering heat resistance	good	good
Tensile strength @ break before aging (kg/cm^{2})	410	420
Tensile strength @ break after 120^{o}Cx7 days aging (kg/cm^{2})	380	380

Reference: H. Hayami et al., "Heat Resistant Engineering Plastic Resin Composition and Molded Article Obtained Therefrom", *European Patent EP1188795A1*, **2002**

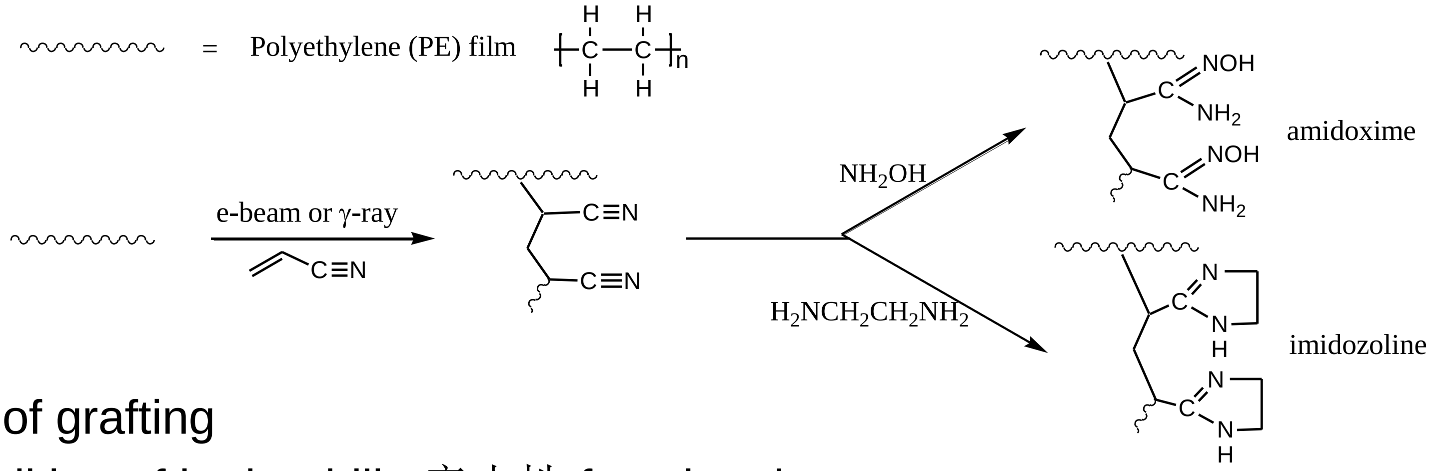
UV Cross-linking of Polyesters 聚酯

- Similar promoters as EB (e.g., TAC, TAIC), but may also need photo-initiator (e.g., difunctional benzophenone)
- UV has penetration limits
- May need elevated temperature

Reference: H. Inata et al., “Postcrosslinking of Linear Polyesters. I – Melt-Blend-Type UV induced Crosslinking Agents”, *Journal of Applied Polymer Science*, 35(7), 1705-1714, **1988**

Examples of Radiation Grafting

Polyethylene films



Effect of grafting

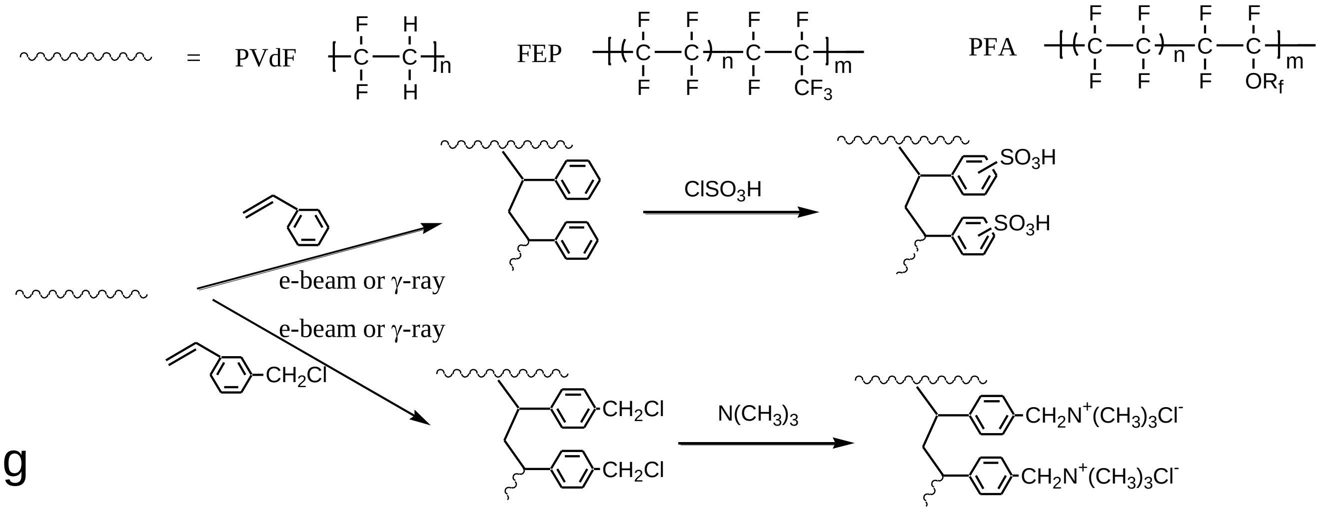
- Addition of hydrophilic 亲水性 functional groups
- Addition of selective permeation properties and ionic conductivity 导离子性, etc.

Applications

- Permeation separation membranes 渗析分离膜
- Fuel cell/battery separator films 电池隔膜
- Surface modification

Examples of Radiation Grafting

Fluoropolymer films



Effect of grafting

- Addition of new functional groups
- Addition of ion-exchange and proton conducting properties

Applications

- Ion exchange membranes 离子交换膜
- Fuel cell/battery separator films
- Surface modification

Radiation Modification of Bulk Polymer Resins

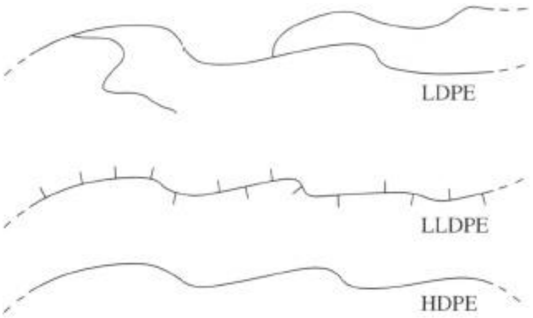
Radiation Processing of Polymer Materials

Modification of polymers can be achieved by radiation processing of the polymer material

- after the conversion / forming of parts – formed parts 成型部件
- before the conversion / forming of parts – bulk polymer resins 高分子树脂

Radiation Pre-processing Modification of Polyethylenes (RAPREX®)

- Applications: Foams 发泡, films 膜材, extrusion 挤出, extrusion coating 挤出涂布, blow molding 吹塑, injection molding 注塑, pipes 管材,
- Base resins: HDPE高密度聚乙烯, LLDPE线性低密度聚乙烯
- Pre-processing modification: radiation induced long chain branching
- Low dose irradiation under ambient conditions (very low gel 凝胶 content)
- Significant processability 可加工性 improvements and possible property enhancements
- Can be blended with un-irradiated resins.
- Radiation is only one part of the whole formula



RAPREX®: Broadened Molecular Weight Distribution

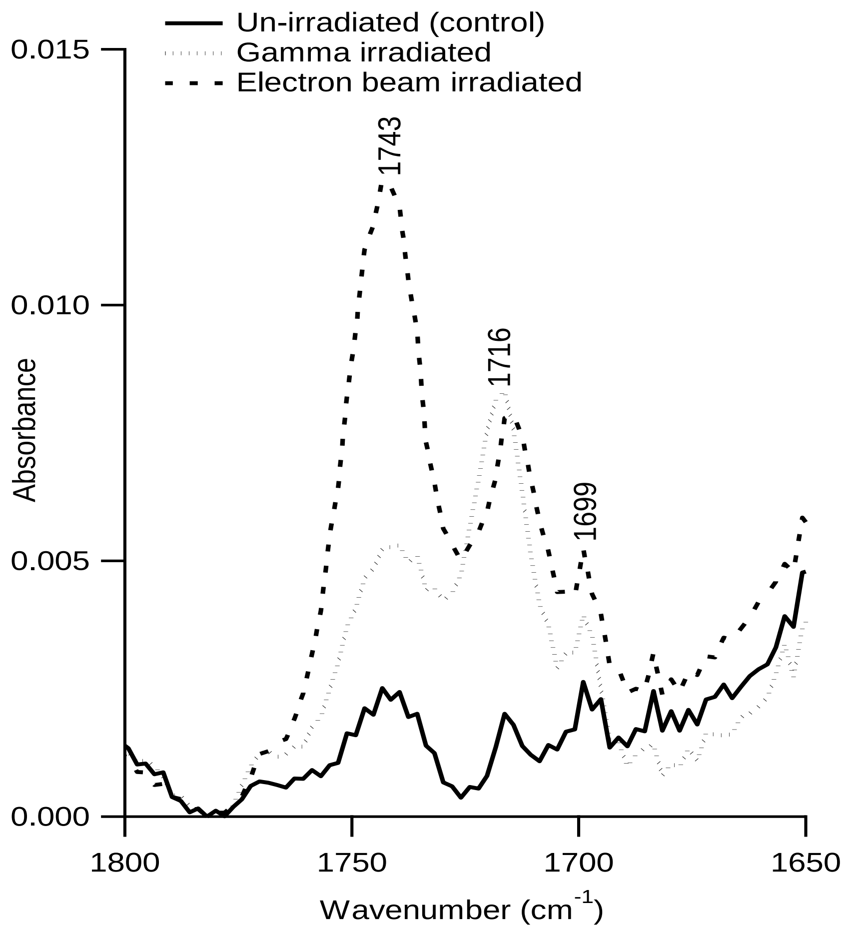
Bimodal Molecular Weight Distribution of Raprex®-200A

Mn: 数均分子量　Mw:重均分子量

EB Dose Level	M_n (Daltons)	M_w (Daltons)	M_w/M_n
0	15452	112093	7.25
Level A	13098	122368	9.34
Level B	11073	158473	14.3
Level C	13035	241912	18.6

Dose level: C>B>A

RAPREX®: New Functional Groups

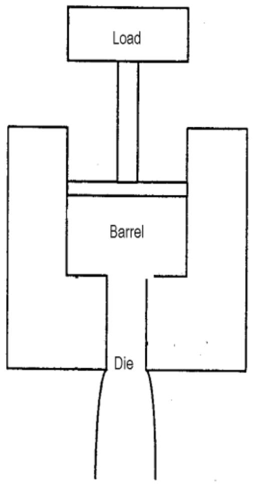


(Carbonyl 羰基 range of the FTIR spectra for Raprex®-200A)

RAPREX®-200: Decreased Melt Flow

Melt Flow Index 熔融指数 of Raprex®-200

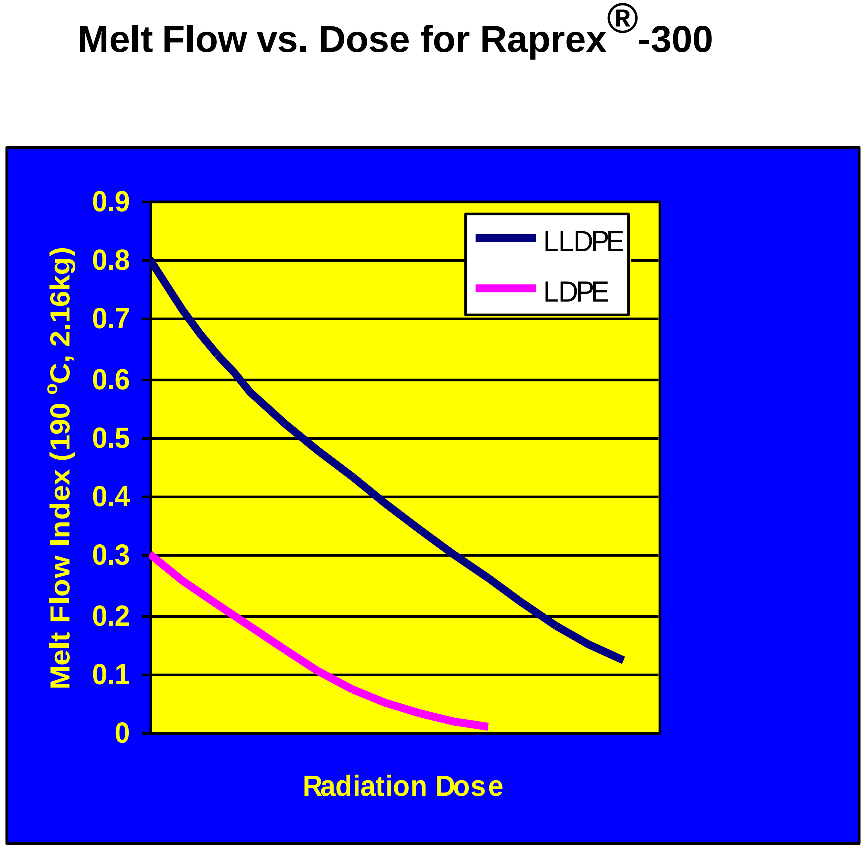
Dose Level	I_2 (g/10 min.)	I_{10} (g/10 min.)	MFRR (I_{10}/I_2)
0	8.65	48.0	5.55
Level A	3.70	31.7	8.58
Level B	0.85	13.6	16.0
Level C	0.12	7.77	64.7



Dose level: C>B>A

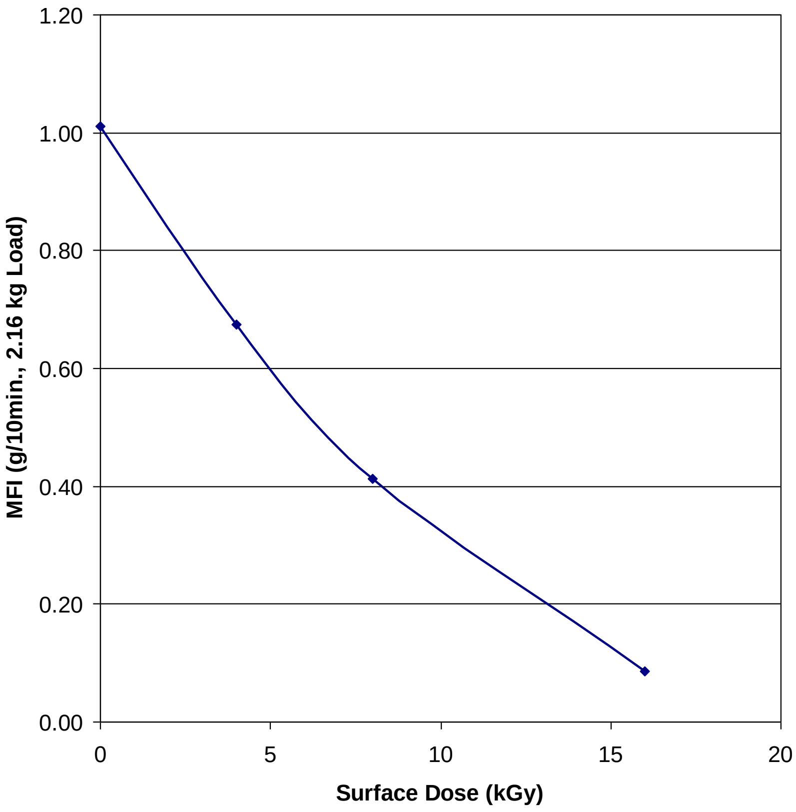
I_2 = 2.16 kg load, I_{10} = 10 kg load, both at 190°C

RAPREX®: Melt Flow "Dial-in"

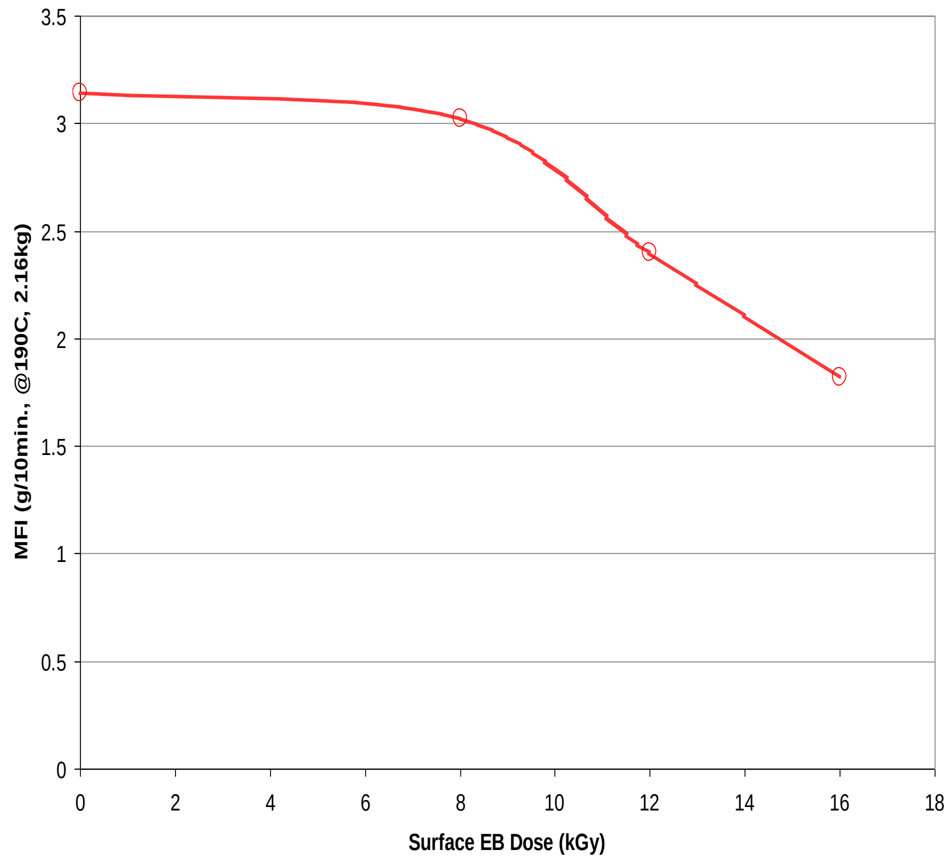


Different MFI vs. Radiation Dose Relationship

IR-300



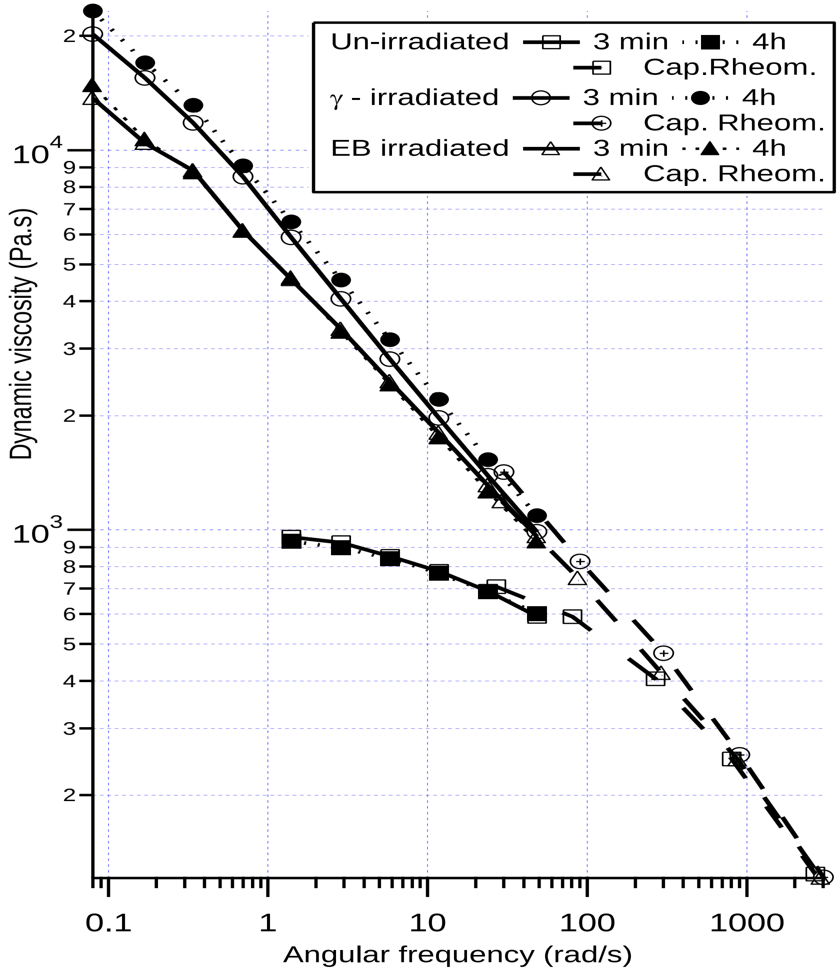
IR-LLD



Raprex® Grades: MFI Changes

Grade	Type	Load	Base Resin MFI (g/10min)	Irradiated MFI (g/10min)
R-100	HDPE	*21.6 kg*	*10.0*	*2.4*
R-200	HDPE	*21.6 kg*	*52*	*13*
R-201	HDPE	2.16 kg	8.6	2.5
R-202	HDPE	2.16 kg	2.0	0.5
R-300	LLDPE	2.16 kg	1.0	0.2
R-301	LLDPE	2.16 kg	4.5	2.0

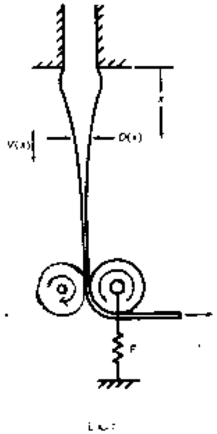
RAPREX®-200A: Increased Melt Viscosity at Low Shear 剪切速度



(Melt viscosity 熔体粘度 data for Raprex®-200A)

RAPREX® R-300 (LLDPE): Melt Strength 熔体强度 Improvement

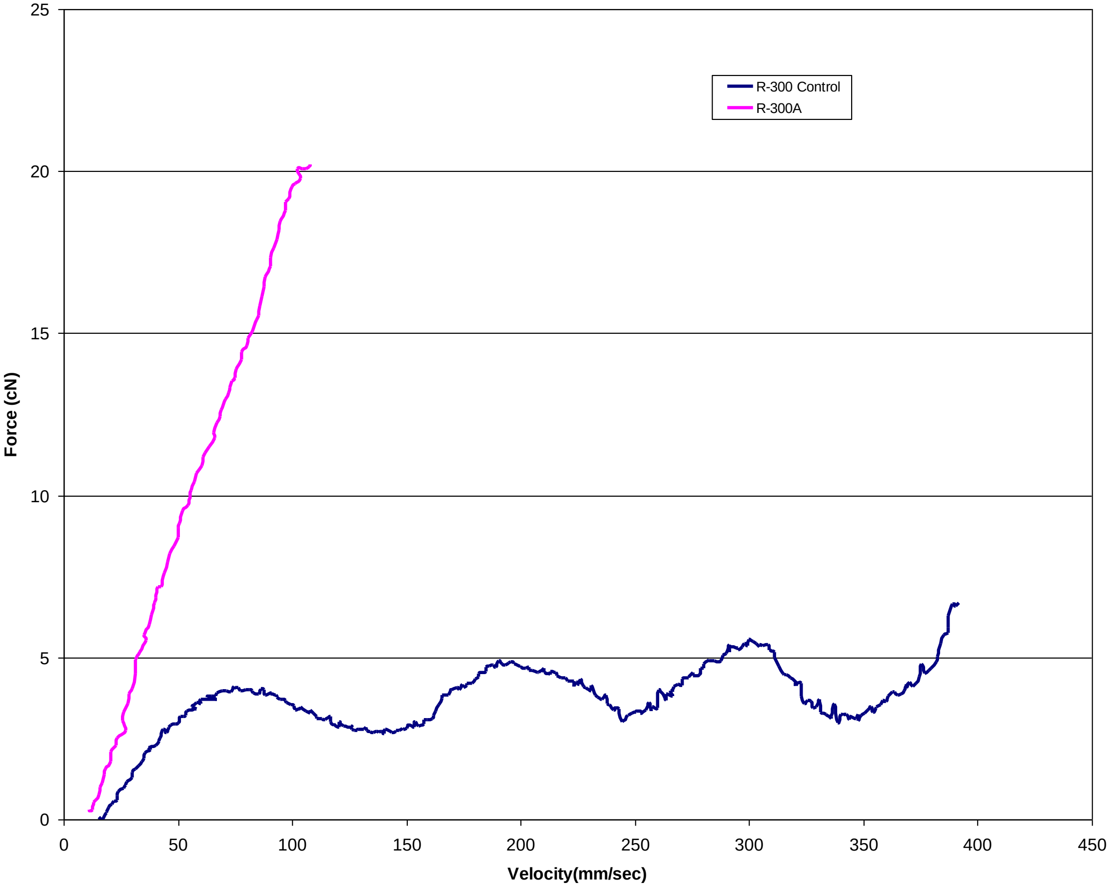
Gottfert Rheotens



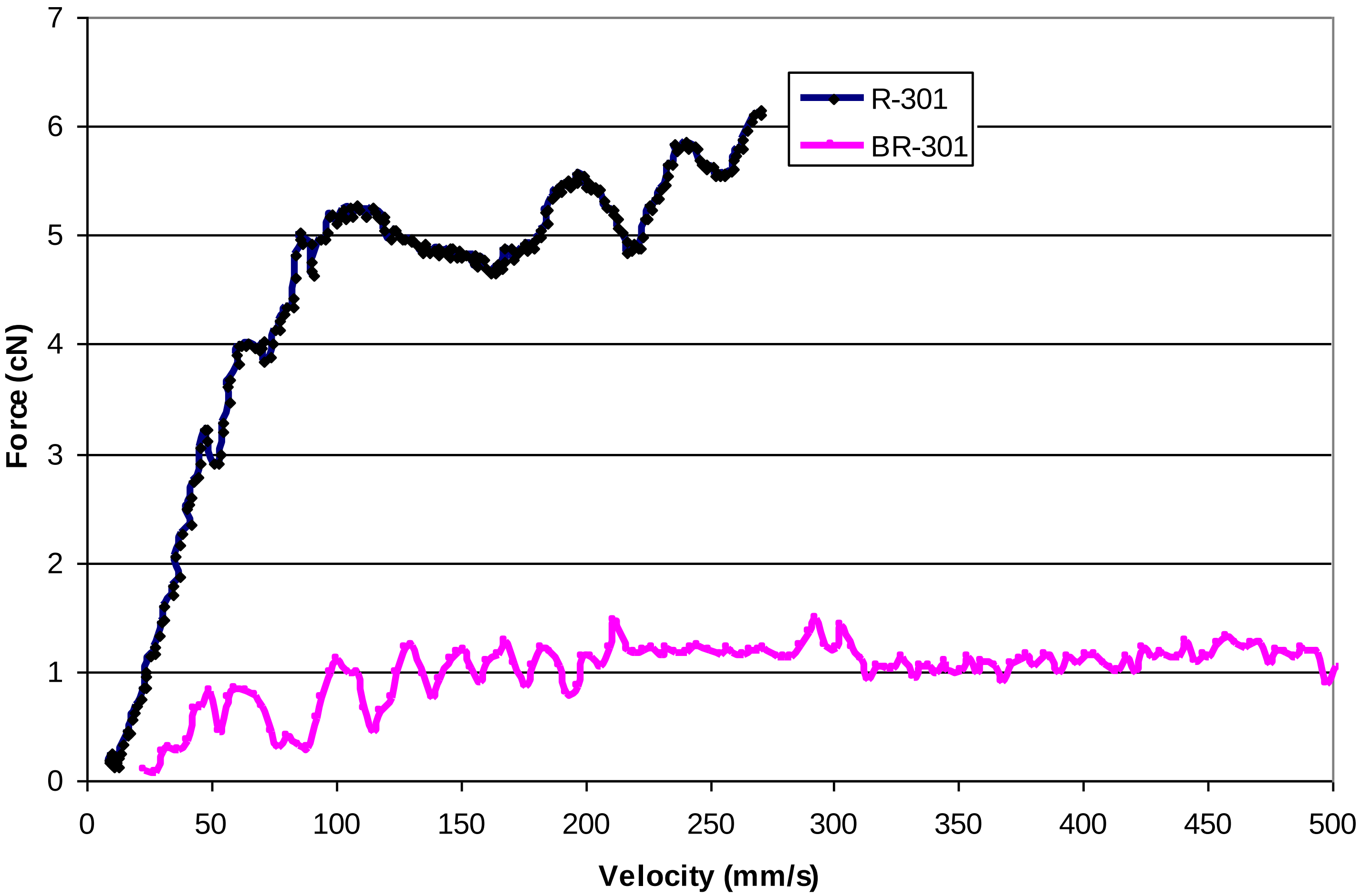
Melt tension (cN) - steady state force at break.
Velocity at break (cm/sec) - extensibility. V_{br} = V_0 + accel. * time.

Advantages:

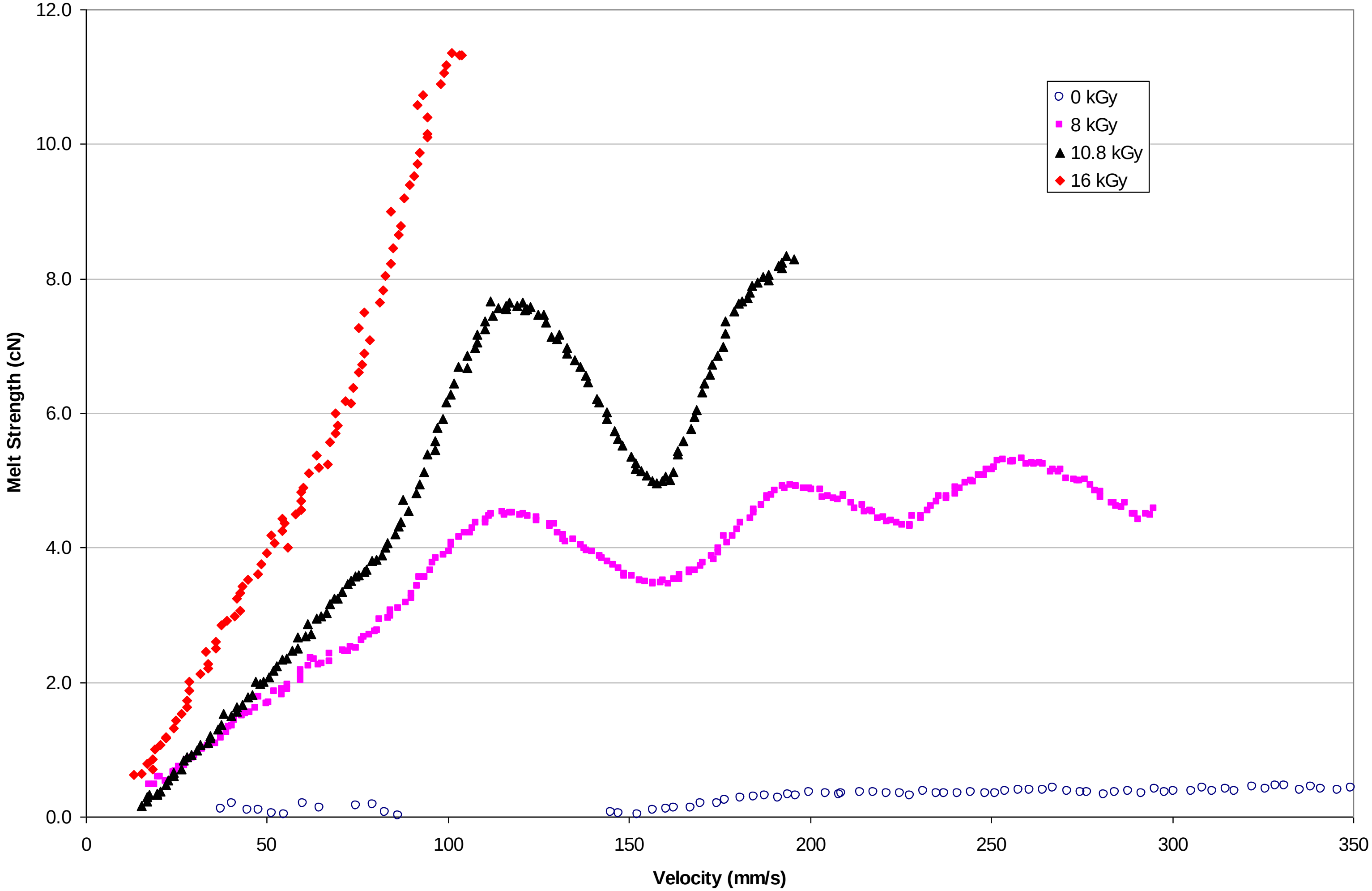
1. Easy to operate.
2. Fast data generation rate.
3. Good reproducibility.
4. Easy to maintain.



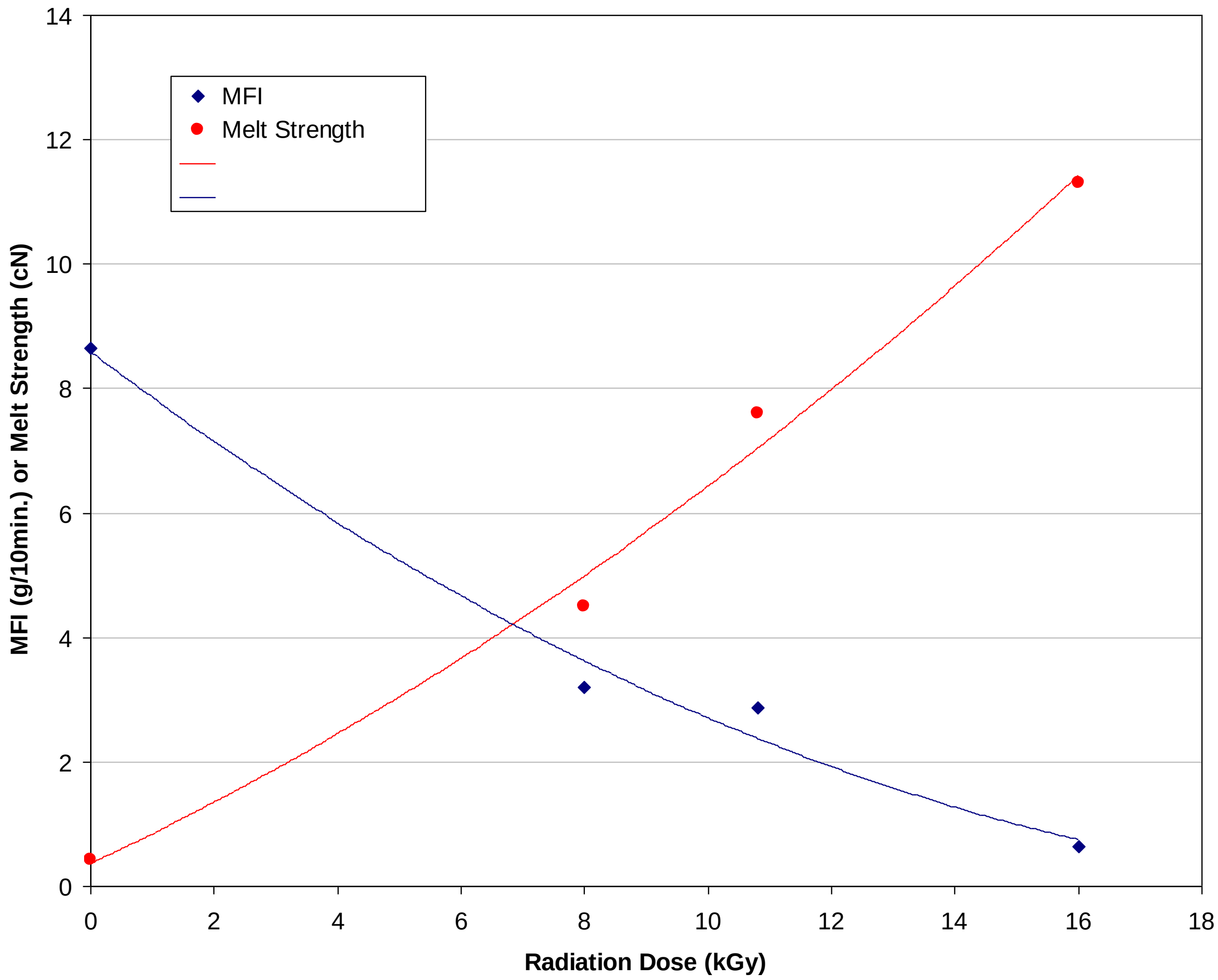
RAPREX® R-301 (LLDPE): Melt Strength Improvement



IR-201 (HDPE): Melt Strength vs. Dose



IR-201 (HDPE): Melt Strength and MFI vs. Dose



Melt Processability Plus Enhanced Physical Properties

- **Low Density Foams**
  - **Supports Uniform Cell Growth**
  - **Higher Heat Resistance**
- **Cast and Blown Films**
  - **Improved Processability**
  - **Increased Puncture Resistance and Barrier Properties**
- **Extruded Pipes, Sheet, Blow Molding and Profiles**
  - **Improved Sag Resistance**
  - **No Shear Thinning / Gauge Uniformity**
  - **Improved Stiffness / Impact Balance = Toughness**
  - **Improved Burst Resistance & Hoop Stress Resistance**
- **Extrusion Coating**
  - **Higher Draw Rates / Ratios**
  - **Higher Heat Resistance**
  - **Improved Surface Characteristics**
  - **Improved Adhesion to Various Substrates**

Raprex = Melt Strength

- **High Zero Shear Viscosity**
  - ***Sag Resistance***
    - Ability of the Polymer to Support Its Own Weight in the Melt Phase
    - Function of Mw, MWD, ***Branching*** or Crosslinking
- **High Extensional Viscosity**
  - **Strain Hardening**
    - Deforms Uniformly
    - High Extensibility
    - Processability at High Draw Ratios / Draw Rates
      - Resists Neck-In and Melt Resonance
      - High Speed Processability
      - Downgagability

Processability & Properties → **Processes** → **Applications & Markets**

- Sag Resistance
  - Extruded Pipes and Profiles
- Strain Hardening
  - Extrusion Coating
  - Cast and Blown Films
  - Low Density Foams
  - Fibers
- BOTH
  - Blow Molding
  - Melt Phase Thermoforming

- Neither
  - Injection Molding
  - Thermo-sprayed & Flocked Coatings
  - Rotomolding

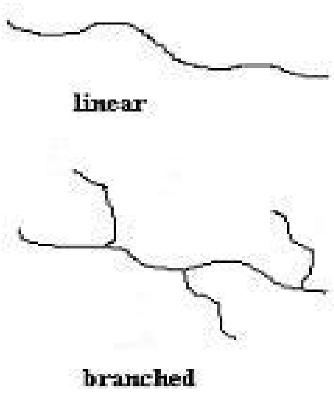
Higher melt strength at Lower MIs = higher throughput where the process is extrusion capacity limited

Radiation Processing of Linear Polyolefins

Branching
||
Apparent Higher Mw
||
Broader MWD
||
Melt Strength
||
Processability

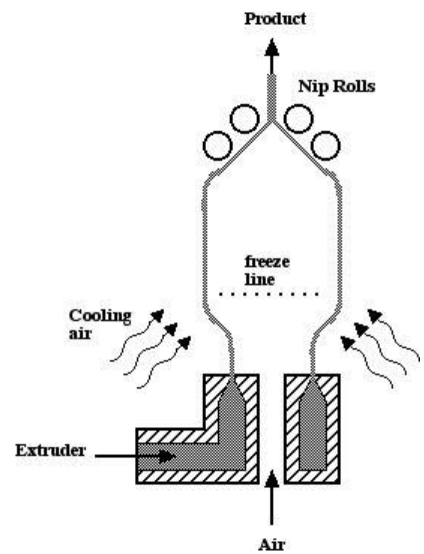
Branching
||
Improved Properties
||
Downguageability
||
Faster Cycling
||
Reprocessability

= Value

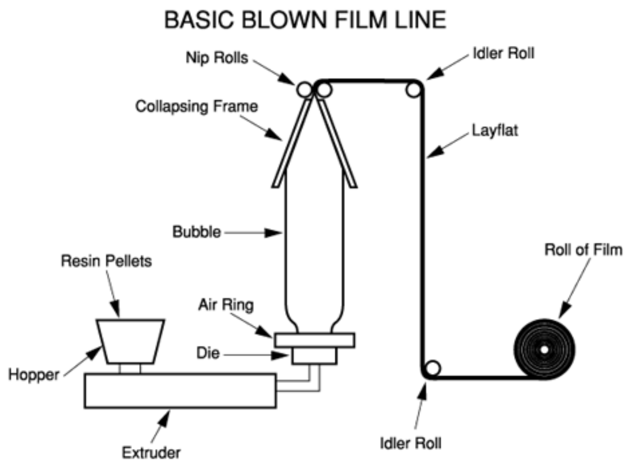


R-300 Film Blowing Processability Advantages

- Higher Blow Up Ratio (BUR)
  - o R-300: 2.0 to 4.0
  - o Un-irradiated control: 2.0 to 2.4
- Improved bubble stability
- Makes it much easier to blow films from 100% LLDPE
- Combines the properties of LLDPE and the processability of LDPE



BUR=(dia. of bubble)/(dia. of die)



R-300 Films: WVTR 水蒸气透过率 Barrier Advantages

May 2006 data

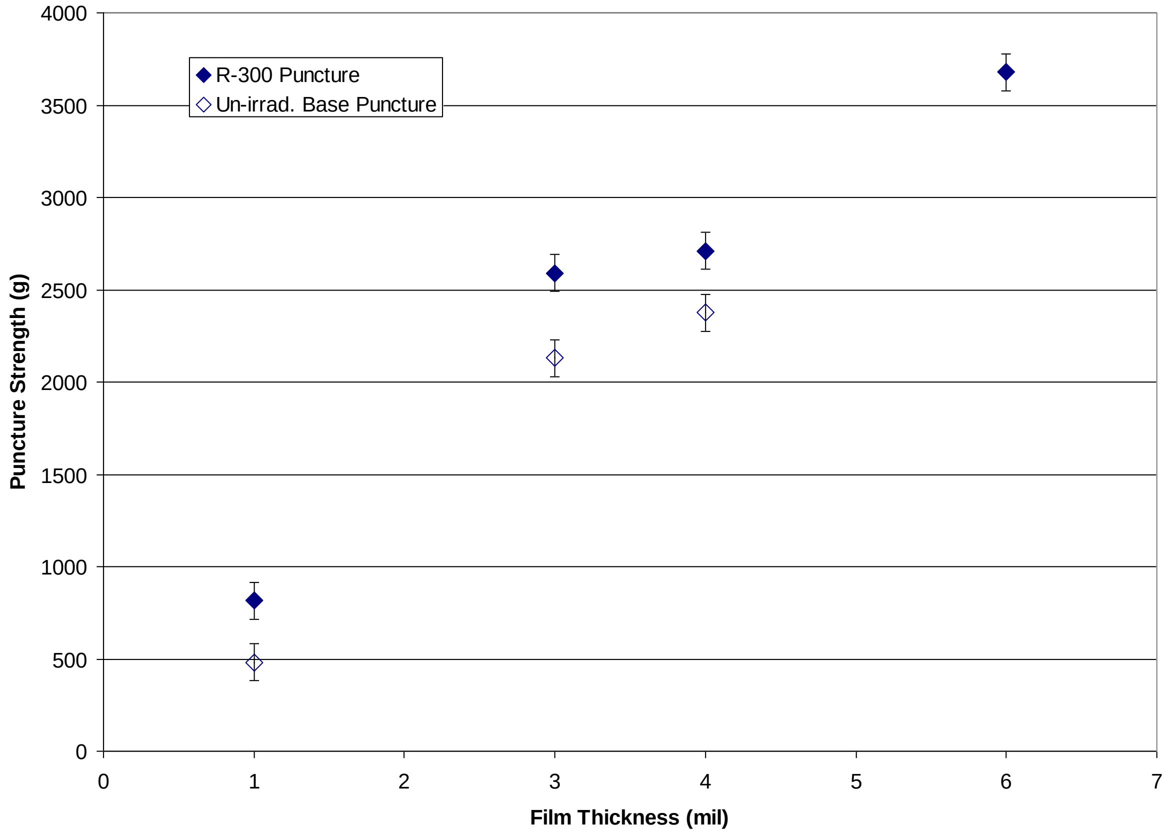
Film Sample ID	R-300 Control Favorite	R-300 Favorite
Film Manufacturer	Favorite	Favorite
Film Thickness	3 mil	3 mil
WVTR (g/hr.m²)	0.035	0.019
WVTR (g/day.100 in²)	0.054	0.029
Normalized WVTR (g.mil/hr.m²)	***0.11***	***0.057***
Normalized WVTR (g.mil/day.100 in²)	***0.16***	***0.083***

All Films tested by STR using ASTM E96 at 73ºF and 50% RH

March 2007 data

Film Sample ID	R-300 Control Profile	R-300 Profile	HDPE 7194 Baxter
Film Manufacturer	Profile	Profile	Baxter's contract
Film Thickness	4 mil	4 mil	4.5 mil
WVTR (g/hr.m²)	0.0160	0.0136	0.0362
WVTR (g/day.100 in²)	0.0245	0.0208	0.0554
Normalized WVTR (g.mil/hr.m²)	***0.0640***	***0.0544***	***0.163***
Normalized WVTR (g.mil/day.100 in²)	***0.0980***	***0.0823***	***0.249***

R-300 Films: Puncture 穿刺 Strength Improvement



However, the Elmendorf tear 撕裂 strength was sacrificed

RAPREX®: Improved Properties

Sample	Resin Type (Grade)	Property	Before Modification	After Modification
Films (1 mil)	LLDPE (R-300A)	Puncture Strength	481 g	921 g
Films (1 mil)	LLDPE (R-300A)	Graves Tear Strength (MD)	7 g/micron	13 g/micron
Films (3 mil)	LLDPE (R-300A)	WVTR	0.035 $g/hr.m^2$	0.019 $g/hr.m^2$
Pipes	HDPE (R-100)	Hydrostatic Stress*	12.4 Mpa	17.4 Mpa
Injection Molded Bars	HDPE (R-200C)	Tensile Strength @ Yield	29 Mpa	39 Mpa

* Gammatron’s data

2006 Foaming Trials

Foams were successfully made from 100% R-300 (1.0-1.5 lb/ft^3) and 30/30/40 R-300/LLDPE/LDPE blend

100% R-300 Foam

30/30/40 R-300/LLDPE/LDPE Blend Foam

2007 Foaming Trials

• 25% R-301 + 75% LDPE blend was used.

• ~2' wide, ~8' ft long, 2.5" thick foam planks were extruded.

• Foam quality depends on the processing conditions. A careful balance of temperatures, pressures and foaming agent content, etc., is important for getting good foams with low open cell content and low density.

RAPREX®: Radiation Is Only One Part of the Whole Formula

Other crucial factors that affect the end-use properties include:

- Selection of base resins
- Effect of additives 添加剂
- Conversion (extrusion, molding, film blowing, etc.) after the radiation modification

Pre-processing Modification of EVA

- Applications: hot melt adhesives 热熔粘接剂, cable and wire, footwear, etc.

- Enhanced properties after modification: mechanical strength and toughness, flexibility, resistance to ozone, oil and environmental stress cracking 环境应力开裂, processability 可加工性

- Modified EVA is used alone or blended with other thermoplastics

Radiation Degradation of PTFE Powders

Effect of degradation

- Decreased molecular weight
- Reduced particle size 粒径 for powders
- Increased melt flow

Applications

- Lubricants and micronized 微米级 powders
- Additives for ink, coating, oil, thermoplastics, etc.
- Synthesis of perfluorinated olefins

Radiation Degradation of PEO (Polyethylene Oxide)

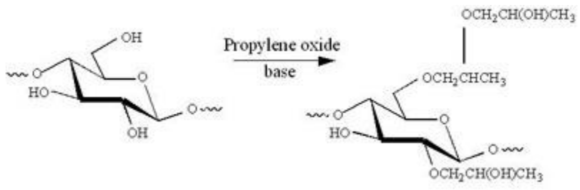
Effect of degradation

- Decreased molecular weight
- Decreased viscosity in solution

Applications

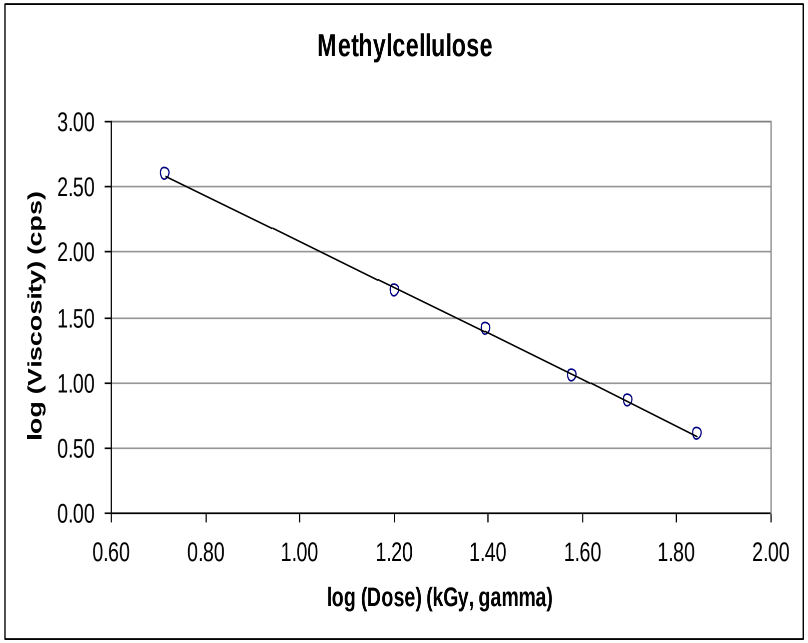
- Drug carrier 载体
- Synthesis of lower MW grade PEO

Radiation Degradation of Cellulose Derivatives (CDs)



(Hydroxypropyl)cellulose (HPC)

- The MW of the water-soluble CD is reduced by radiation degradation to make lower MW grades where it is difficult and too expensive to make the lower MW grades from reactors.
- The concept can be applied to water-soluble CDs such as MC, HPMC, CMC, EHEC, MEHEC, cellulose ether, cellulose acetate, etc.
- Reduction of MW would decrease the viscosity of the CD's solution in water, and may also increase their solubility in water.
- Chemical methods were used in the past to reduce the MW of water-soluble CDs, but the process was uneconomical and environmentally unfriendly.



T. A. Chamberlin, et al.(Dow Chemicals), "The Degradation of Methylcellulose by Ionizing Radiation",

Macromolecules, 2(1), 88-93, 1969

Production of Rayon Textiles from Viscose

Reduction in chemicals (NaOH, CS_2), time and cost for viscose production

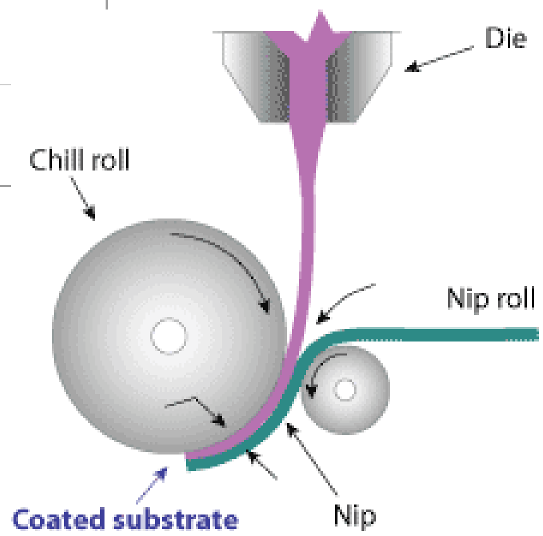
Pre-processing Modification of Polypropylene (PP)

- Controlled degradation
- Processability improvement
- Application in melt processing (e.g., extrusion, melt coating)
- Increased melt flow rate
- Enhanced melt strength (oxygen-free atmosphere needed)
- Improved adhesion
- Irradiated polymer may be blended with un-irradiated one

Pre-processing Modification of Polypropylene (PP)

Application: Extrusion Coating 挤出涂布
Significant branching with controlled active O_2 content (<0.1 vol%)

Polypropylene Resin	Linear	Irradiated-I	30% Irradiated-II + 70% Linear
MFR (10g/min.)	35	34	47
Max. Coating Speed (m/min.)	107	213	244
Neck-in*	15.5	2.5	3.8



Irradiation dose: 80 kGy

* Defined as the difference between the die width (40.6 cm)

and the final coat width

Source: U. S. Patent 4,916,198, Himont Incorporated, 1990

Pulvguard: PP Powder for Powder Coating 粉末涂敷

- Sterigenics-Dyvex joint project.
- Process: irradiate PP pellets (for increasing MFI and keeping melt strength)→compound the pellets (with additives)→grind the pellets into powder.
- Formulation (service to 100^{o}C):

PP Powder 101	
PP Homopolymer	聚丙烯
PP Copolymer	聚丙烯共聚物（抗冲击性）
PP-MAH	马来酸酐接枝聚丙烯
Antioxidant	抗氧剂
UV Stabilizer	光稳定剂
Calcium Stearate	加工助剂
TiO_2	白色颜料
DSTDP	硫醇（热稳定剂）

(2007 Formulation)

Pulvguard: Basic Properties

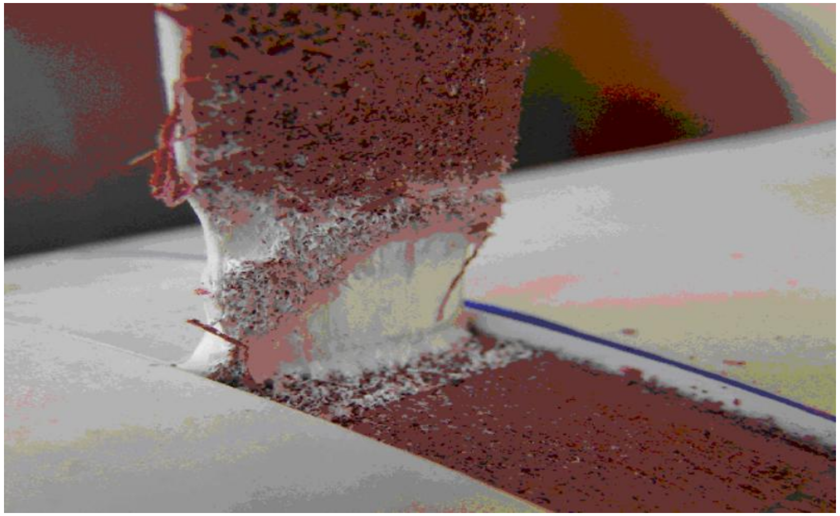
Property	**Standard**	**Unit**	**PP-101**	***EP5 10/60 Bianco****
Melt Flow Index (230ºC, 2.16kg)	ASTM D1238	g/10min.	27.8	*9.0*
Density	ISO 1183	g/cm^3	0.908	*0.900*
Tensile Strength @ Yield	ISO 527	MPa	20.2	*16*
Elongation @ Yield	ISO 527	%	12	*ND*
Tensile Strength @ Break	ISO 527	MPa	No break	*ND*
Elongation @ Break	ISO 527	%	>500	*>400*
Flexural Modulus	ISO 178	MPa	836	*700*
Izod Notched Impact Strength at Room Temperature (23 ºC)	ISO 180	kJ/m^2	7.9	*ND*
Izod Notched Impact Strength at -20 ºC	ISO 180	kJ/m^2	5.3	*ND*
Vicat Softening Temperature	ISO 306	ºC	128	*ND*

* Basell commercial product, for comparison

Pulvguard: Excellent Adhesion (Peel Strength)

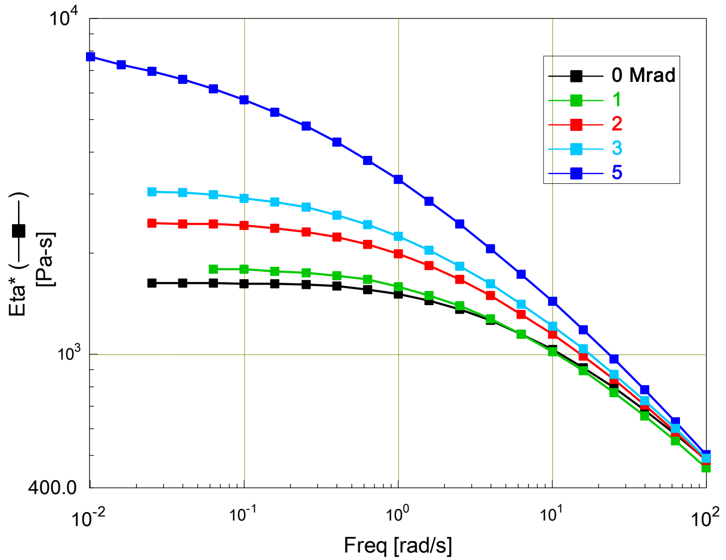
Temperature	DIN Spec. (minimum)	Measued
(oC)	(newtons/cm)	(newtons/cm)
30	>100	250-275
50	100	196
90	80	114

(Data Source: Ball Winch)

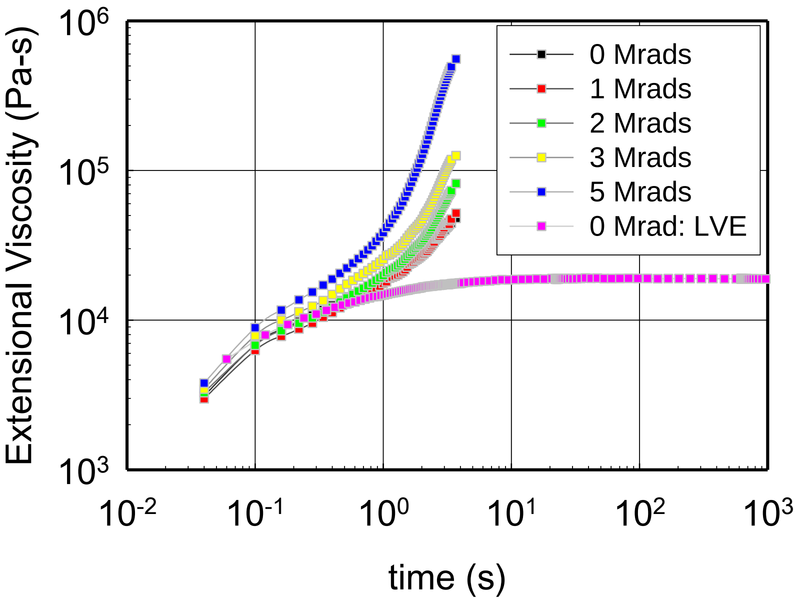


PVdF Rheology Modification

Kynar® 710



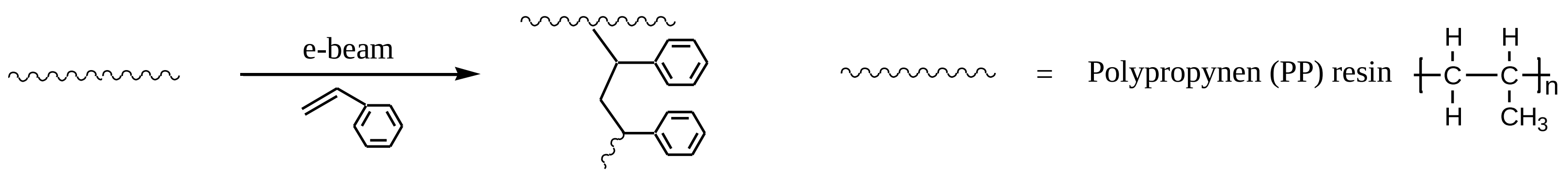
Melt Viscosity



N. Mekhilef et al, SPE ANTEC presentation, Cincinnati. OH, May 2007

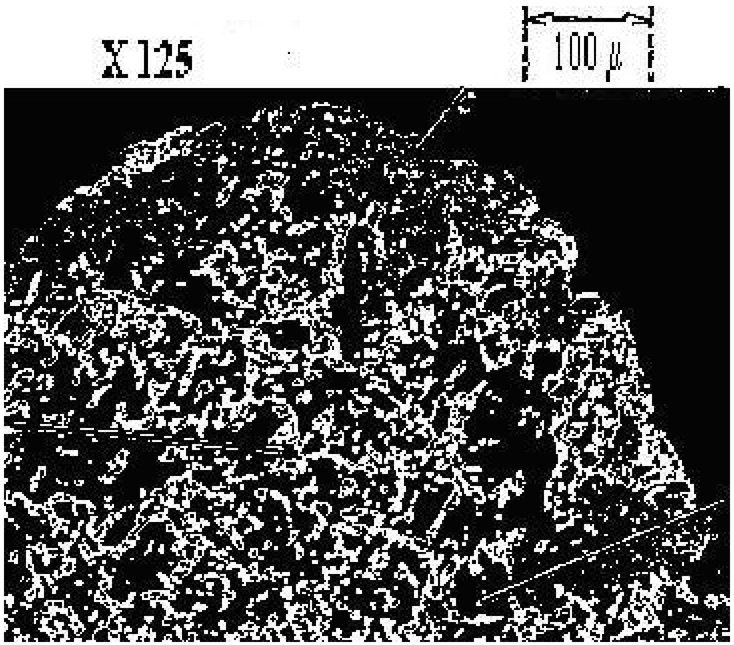
Grafting on Polypropylene (PP) Pellets

- Modification of bulk polymer properties
- Application: compatibilizers for polymer blends or inorganic fillers, plastic modifiers, etc.
- Pre-irradiation grafting of vinyl monomers
- Non-oxidizing atmosphere to prevent degradation
- Deactivation of residual radicals and removal of unreacted monomers

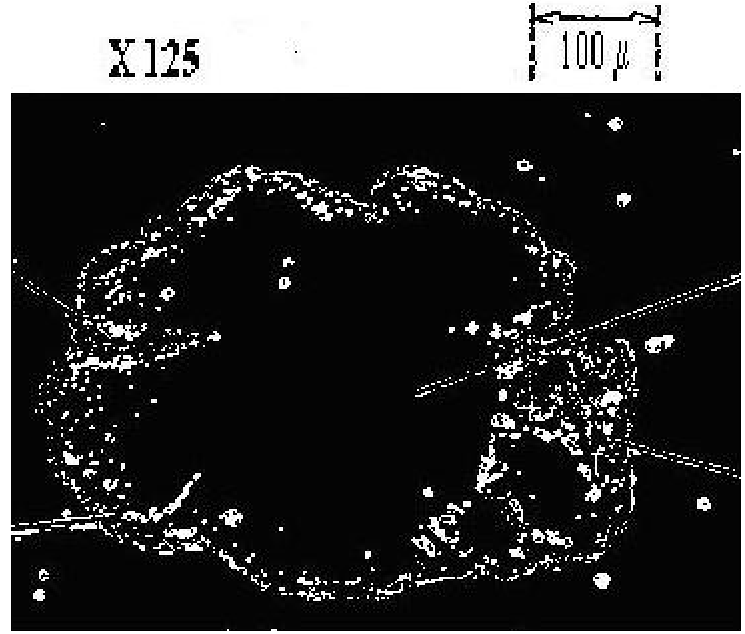


Grafting on Polypropylene (PP) Pellets

Microtomed Photomicrography of Cross-section of Styrene Grafted Polypropylene Particles



Radiation Grafting



Chemical Grafting

Source: U. S. Patent 5,411,994, Himont Incorporated, 1992

Questions?

… to be continued