ADHESION PROMOTING OLIGOMERS FOR INDIRECT FOOD PACKAGING

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AGENDA

- Flexible food packaging market
- Challenges in flexible food packaging
  - Barrier properties
  - Migration
  - Adhesion
- Global regulatory challenges
  - Sartomer strategy for in-direct food packaging (LM)
- Adhesion Fundamentals
- Adhesion promoting oligomers for in-direct food packaging
- Conclusions

FLEXIBLE FOOD PACKAGING

- **Driven by consumer and manufacturing demand for smaller, more lightweight packaging**
  - Saves on product transportation
- **Shelf life, functional barriers and package re-sealability have greatly improved**
- **Trend is transitioning from rigid containers to flexible packaging**
  - Combination of market cannibalization and new flexible packaging

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MARKET FOR FLEXIBLE PACKAGING

- **US flexible food packaging 71% of total flex demand in 2016** [1]
- **Expected to rise to $15.5 billion in 2021.**
  - 65% of food packaging demand:
    Meat/poultry/seafood, baked goods,
    snack food, produce, candy/confections, and pet food[1]

- **Global packaging (conventional/UV) estimated to be $950 billion[2].**
  - Asia ~36% of the market, North America and Western Europe ~ 23% and 22%, respectively
  - Considerable growth is in the flexible packaging segment

- **Translates into $8 billion of the $20 billion global ink (conventional/UV) market**
  - Flexo, gravure, sheetfed inks, digital printing steadily growing[3]

1. Market study, "Converted Flexible Packaging Market in the US, 14th Edition," by The Freedonia Group
2. SmithersPira ("The Future of Global Packaging to 2018") https://www.inkworldmagazine.com/issues/2015-05-01/view_features/packaging-inks-market
3. https://www.inkworldmagazine.com/issues/2017-05-01/view_features/the-packaging-ink-market-continues-to-thrive

CHALLENGES IN FLEXIBLE FOOD PACKAGING

→ **Related to polyolefin and polyester used for the pouch or container body**

- Moisture and oxygen diffusion
- Mitigated by lamination of several polymer substrates or metal foils.

→ **Migration potential of printing inks**

- Exclude low molecular weight components
- Ensuring the highest degree of cure
- Lamination of functional barriers
- Low migration criteria will be explored later

→ **Adhesion of printing inks remains one consistent challenge**

- Mainly attributed to the low surface energy of the polymer base
- Poor solubility of polyolefins in monomer, no interpenetrating network formed

ADHESION CHALLENGES IN FLEXIBLE FOOD PACKAGING

GENERAL FILM MATERIALS	ABBREVIATION	Surface Energy (mJ/cm2) [4]
Polypropylene	PP	30
Cast Polypropylene	CPP	30
Low Density Polyethylene, Linear Low Density Polyethylene	LDPE, LLDPE	31
Oriented Polypropylene	OPP,BOPP,MET-BOPP	31
Polyethylene	PE	34
High Density Polyethylene	HDPE	35
Polyethylene terephthalate, Metalized PET	PET, METPET	44
Polyamides	PAM	44

- **Diversity in polymer attributes**
  - Flexibility/Rigidity
  - Moisture and oxygen barriers
  - High/Low temperature resistance
- **Surface energy increases, adhesion properties generally improve**
- **Table illustrates abundance of low surface energies**
- **Corona/plasma treatment improve adhesion**
  - Not always enough/ available

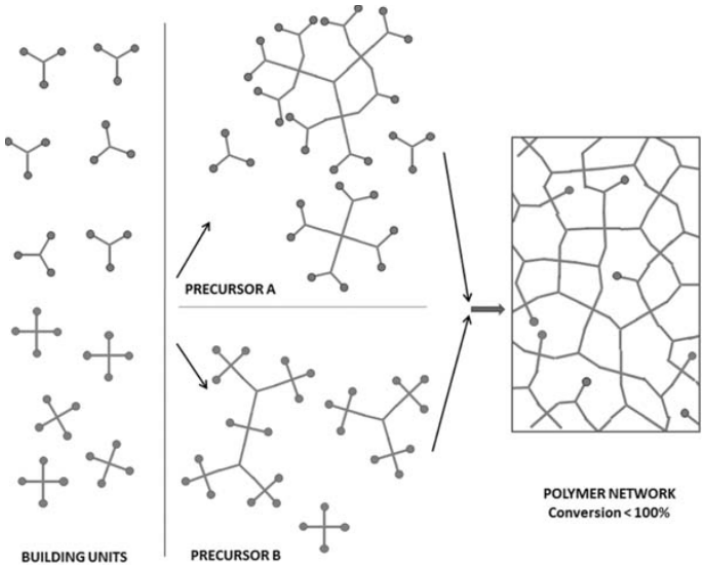
4. https://www.accudynetest.com/polytable_01.htmlc

GLOBAL REGULATORY CHALLENGE

- U.S. Federal Food Drug and Cosmetic Act (FFDCA) requires that packaging will not adulterate any human /pet food
- FDA requires that chemicals that migrate into food are considered indirect food additives
  - Subject to FDA Food contact substance (FCS) in parts 174-186 of Title 21
  - Levels must be below threshold of regulation (TOR)
  - Food contact notification (FCN) process
- Compliance with EU for indirect food packaging
  - 2005 Swiss Ordinance, SMLs (Migration Limits)
  - 2016 Nestle guidance note, Exclusion/Minimize Lists

SARTOMER'S LOW MIGRATION STRATEGY

- **Low potential for migration >400g/mol**
  - Higher purity monomer diluents
- **High functionality monomers (≥3)**
  - Optimizes crosslink density
  - Can work against adhesion
- **Reduce cross contamination and NIAS* through production sequencing**
- **Printer is responsible to prove packaging migration specifications**
  - Migration limits (SMLs) dictated by Swiss Ordinance
  - Extensive migration testing, based on Swiss protocols
  - Worst case scenario calculations



*Not Intentionally Added Substance

ADHESION FUNDAMENTALS

Important relationship between stress and adhesion[5]

Stress intrinsic to coating

- S^F = crosslink density, shrinkage due to Δ free volume
- S^T = Thermal expansion and Tg difference between coating/substrate
- S^H =Hygroscopic expansion

$$S = \frac{E\epsilon}{1-\nu} \quad (1)$$

$$S^F = \frac{E}{1-\nu} \cdot \frac{\Delta V}{3V} \quad (2)$$

$$S^T = \int_{T_1}^{T_2} \frac{E}{1-\nu}(\alpha_F^T - \alpha_S^T)\,dT \cong \frac{E}{1-\nu}(\alpha_F^T - \alpha_S^T)(T_g - T) \quad (3)$$

$$S^H = \int_{RH_1}^{RH_2} \frac{E}{1-\nu}(\alpha_F^H - \alpha_S^H)\,dRH \quad (4)$$

The total sum of stresses can indicate impact on adhesion

- Positive number indicates tendency to shrink
- Negative number indicates coating expansion

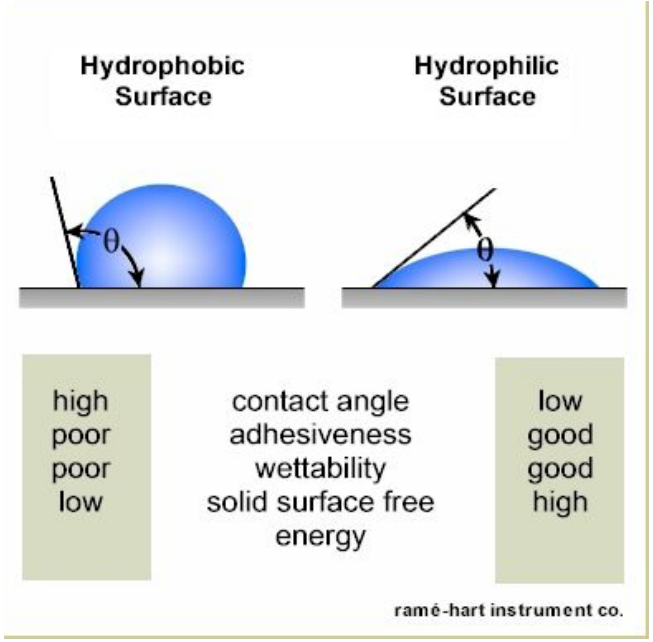
$$S_{tot} = S^F \pm S^H \pm S^T$$

5. Perera, D. Y. (1994). On Adhesion and stress in organic coatings. *Progress in Prganic Coatings*, *28*(1996), pp. 21-23.

ADHESION FUNDAMENTALS

- **Surface energy, free energy per unit surface area**
  - Energy to determine substrate wetting
  - Lower energy for hydrophobic surfaces
- **Surface Tension, force that "hold a fluid together**
  - Determines if ink will wet and spread/ retract from solid surface
  - Lower energy for hydrophobic liquids
    - HDDA ~ 36 dynes
    - Alkoxylated HDDA ~39 dynes

Lower Contact Angle = Better Adhesion



ADHESION FUNDAMENTALS

Substrate Surface Energy > Ink surface Tension

- **Typical ink surface tension 30-40 dynes**
- **The larger the difference in Surface Energy (γ_S)and Surface Tension (γ_L) better the adhesion**
- **Even with corona treatment, adhesion can be difficult !**

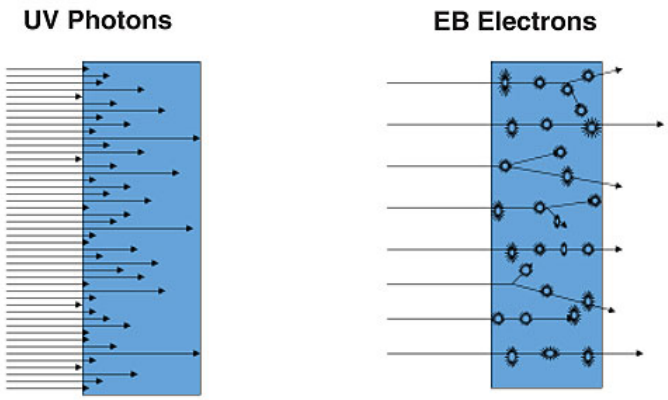
Typical Treat Levels & Watt Densities[6]			
	Incoming Level	Desired Level	Watt Density
Treated BOPP	34 – 36	40 – 42	2.5 – 3.5
Treated BOPET	40 – 42	54 – 56	0.9 – 1.5
Treated LDPE, high slip	34 – 36	40 – 42	2.5 – 3.5
Cast PP, no slip	38 – 40	40 – 42	1.5 – 2.5
Untreated LDPE, low slip	30 – 31	no data	no data

Note: Variations in resin blend, additives or process will affect values.

6. http://www.accudynetest.com/blog/corona-treater-output-vs-increase-in-dyne-level/

ADHESION FUNDAMENTALS: EBEAM

- e⁻ much higher energy then photons
- The electrons cut molecules, forming radicals
  - chain-scission, mechanism behind sterilization, polymer degrading
  - ebeam reduces molecular weight by chopping long chains into shorter chains
- Electron beam-induced reactive compounding (grafting)
  - Electron grafting, cut and paste
  - Enhances adhesion of inks and coatings to various substrate



NEW ACRYLIC OLIGOMER

Physical Properties

- Appearance: Clear Liquid
- Color, APHA: 23
- Refractive Index: 1.483
- Tg °C (by DMA): 46
- Viscosity, cP @ 60 °C: 5000

Product Attributes

- High MW/Low Shrinkage
- Nestle/Swiss Compliant
- 550 fpm cure speed, D bulb
- Balance Hydrophilic/Hydrophobic

Applications

- Lithographic Inks
- Flexographic Inks

	PE	PP	PC	PET	PETG
New Acrylic Oligomer	0	25	100	75	100
Corona Treatment	*100*	*100*	*100*	*100*	*100*

Adhesion Tape Test: Adhesion and cure evaluation at 50/50 (3EO)TMPTA/Acrylic Oligomer dilution, PI 50/50 TPO/BAPO, LED 395 @50fpm

NEW POLYESTER ACRYLATE OLIGOMER

Physical Properties

- Appearance: Clear Liquid
- Color, APHA: 34.5
- Tg °C (by DMA): 57
- Viscosity, cP @ 60 °C: 2400

Product Attributes

- Low Shrinkage due to high molecular weight
- Nestle/Swiss Compliant
- 550 fpm cure speed, D bulb
- Hydrophobic characteristics

Applications

- Lithographic Inks
- Flexographic Inks

	PE	PP	PC	PET	PETG
New PEA Oligomer	50	100	100	100	50
Corona Treatment	*100*	*100*	*100*	*100*	*100*

Adhesion Tape Test: Adhesion and cure evaluation at 50/50 (3EO)TMPTA/PEA Oligomer dilution, PI 50/50 TPO/BAPO, LED 395 @50fpm

CONCLUSIONS

- **Considerable growth in the flexible fooe d packaging segment**
  - Translates to growth in the global ink market
- **Strategies for overcoming challenges in flexible food packaging**
  - Functional barriers for moisture & oxygen diffusion and ink migrate-ables
  - Minimize low MW components
  - Highest degree of cure
- **Strategies on optimizing adhesion to polyolefin/polyester flexible films**
  - Reduce shrinkage and thermal strain
  - Align Tg of coating with substrate
  - Ensure Surface Energy > Surface Tension, corona treatment beneficial
- **New acrylic and polyester acrylate oligomers developed to meet all these challenges**

THANK YOU FOR YOUR ATTENTION
QUESTIONS?