

Ink Jet Tubing Application Requirements, Material Selection and Processing

Donald G. Curran Saint-Gobain Performance Plastics, Fluid Systems, Process Systems, Mickleton, NJ 08056

Abstract

Air bubble growth can be detrimental to ink jet print head functioning. The proper selection and combination of barrier materials allows for minimal bubble growth. Complimentary functional and processing properties and characteristics must be considered in the design of ink jet tubes for a successful application.

Introduction

Higher resolution ink jet printers require less mass on the traversing carriage and lower changing inertia as ink is consumed to achieve high print quality and low target costs for economic printer component parts. These new targets have necessitated design to evolve to remote ink cartridge storage with plastic tubes feeding the printer head. Issues that must be addressed with this new set of requirements are permeation, air bubble growth, tubing flexibility for minimal carriage movement power and torque requirements, fitting retention and creep, chemical compatibility with ink components, additives such as plasticizers and flame retardants and migration problems associated with them, tie layers, process capability, wall concentricities and diameter control and the effects of orientation. All tubing must be consistent and precise related to inside and outside diameter, wall thickness and individual layer and concentricity control with the absence of flaws and gels.

Barrier Materials

Water from water based inks used in ink jet printers will permeate through / exit from the plastic tubing wall and be replaced by air, atmospheric nitrogen and oxygen, forming long bubbles. If too long, the bubble will interfere with the proper start up of the printer head. Thus, the prevention of liquid or gas permeation through a plastic cross section is a highly desirable property. Similar problems exist in food, drug, medical device and microelectronics industries that use film or tubing to protect or transfer highly sensitive materials and are concerned about material loss, compositional changes or contamination issues that can occur when gasses or liquids permeate in or out of their protective container or transfer tubing.

To address this need, a complete understanding of the permeation mechanism, material options and processing techniques is essential.

The mechanism for permeation for gasses that obey Henry's Law (gas to liquid at non normal temperature and pressure) is explained by Fick's First Law:

$$V = P \cdot (A \cdot p \cdot t) / s, \quad (1)$$

V, volume; P, Coefficient; A area of wall; p, partial pressure differential; t, time; s, wall thickness

Fick's First Law for gasses that do not follow Henry's Law, liquid at "normal" temperatures is.

$$W = VTR \cdot (A \cdot t) / s \quad (2)$$

W, weight of penetrant; VTR, vapor transmission rate. [1]

The movement of gas through polymers (permeability) is actually made up of two components comprising solubility and diffusivity. . When a film or tube separates two areas with gasses at different partial pressures, the permeability of the film or tube to the gas can be described by a permeability coefficient which is described by the equation,

$$Q = P (\Delta p / l) \quad (3)$$

where Q is the mass of the penetrant passing through a unit area (of the film thickness or tube wall thickness, metric or inches) per unit time with Δp being the difference in partial pressure across the film or tubing wall thickness and l is the film or tubing wall thickness. (The Δ is the driving force for the movement of the gas.) "P" is the permeability coefficient or simply the permeability. Gasses pass through the film or tube wall of given polymers by dissolving in the polymer at the high – pressure side and passing through the film or tube wall thickness by diffusion. First there is a condensing of the gas vapors, then the dissolving into the polymer, diffusing through it and again vaporizing from the exiting surface. In the absence of special barriers through the surface, the rate determining step is the passage of the gas via diffusion within the polymer. [1]

$$P = D \cdot S \quad (4)$$

Also generally accepted is the increase in D with increasing temperature and molecular size. Additionally, increase in crystallinity and degree of cross linking both decrease permeability. Although diffusivity may be more dependent upon the molecular weight of the gas, overall permeability is tempered by the solubility of the gas, for example, low molecular weight hydrocarbons, Methane vs. Propane through polyethylene. Although methane is smaller, its permeation rate through PE is .28 vs .69 cc/cm sec atm of propane through PE due to the greater solubility of the propane in the polyethylene. [2] See Table 1.

Ideal material combinations consist of polymers that are good air barrier, good water barrier materials and tie layer materials. Supporting functional properties must also be considered.

Families of materials include fluoropolymers, nylons, polyolefins, and pvc/pvdc resins etc. See Tables 2 and 3.

Discounting cost, some of the best materials of choice for low barrier objectives are Polyvinylidene chloride, PVDC and Polychlorotetrafluoroethylene, PCTFE. (Used liberally in other markets mentioned above.) Initially these best barrier materials may be attractive but upon review of all of the costs, production and physical property stability issues the need for an understanding of all available barrier materials and combinations is apparent.

Polyvinylidene chloride, PVDC with it's very low water vapor transmission rate of 0.01 -0.08 g x mm/m² x day and .015- .- 0.2533 cm² mm/m² day atm Oxygen Transmission rate is an inexpensive material but is difficult to process. PVDC is very unstable at its processing temperatures leading to degradation and carbon showers after limited production processing time even after process optimization. [3]

Polychlorotetrafluoroethylene, PCTFE, .015 g mm/m² day MVTR, 4.457 cm² mm/m² day atm (must be processed addressing its low Tg and potential brittleness). Additionally, properties change when exposed to temperatures above its Tg will change its flexibility even if it was properly manufactured to optimize properties. Aclar PCTFE-VDF copolymer and PCTFE films are still widely used in packaging where physical properties are not as important as they are in a dynamic tube application.

With all of the problems associated with these ideal barrier candidates coupled with economic considerations, alternative engineered products must be investigated. Other "superior" barrier materials include polyvinyl alcohol, PVOH, ethylene vinyl alcohol, EVOH, moisture sensitive cyclic olefin copolymers, COC and liquid crystal LCP each with their own problems of stiffness's up to 600,000 psi and brittleness associated with that. EVOH is moisture sensitive with very low gas permeability increasing with increasing relative humidity.

Nylon materials, relatively stiff with Flexural moduli of between 180,000 and 400,000 psi depending upon their chemical /monomer make up, 6, 66, 610, 6/12, 12 and level of moisture absorption, 12 having one of the lowest at 0.7% by weight at equilibrium with 50% R.H. [4] , have a low permeability to air and high permeability to water and other polar substances. They are also used as food packaging materials but must be used in thin wall cross sections or in conjunction with plasticizers or ether block amide systems to minimize their effect on tubing stiffness. The compatibility of the plasticizer with the ink must be evaluated. Polyamides are normally married to polyolefins to make up for the poor moisture barrier properties of the nylon. (Water is an inherent part of nylon chemistry.)

Polyolefins, polyethylenes and polypropylenes, have relatively low moisture vapor transmission rates at between .35 and 1.25 grams mil/100 in 2 24 hr 100 F with the stiffer higher density materials, .93 to .96 g/cm³, having the lowest permeation and low density materials, greater flexibility but slightly elevated MVTRs. They are however high in gas transmission. Polypropylene, PP is mainly produced cast as unoriented PP, UPP, and oriented PP, OPP. However, PP has low temperature resistance and impact property problems so its use in inkjet tubing has been limited. (Also, with comparable stiffness, HDPE has MVTR of .35 with Homopolymer PP being .5 g ml/100 in² 24 hr 100 F)

Even more flexible options include Ultra low density polyethylenes, ULDPE, (Dow ATTANE), Ethylene Vinyl Acetate, EVA, Polyolefin elastomers, (Dow Engage). These highly flexible materials have moderately low M/WVTRs To deal with dissimilar chemistry of the barrier polymers, some times "tie" layers, modified with maleic anhydride or similar chemistry are used to enhance bonding between the materials like nylon and polyethylene.

Ever increasing demands for decreased permeability are pushing the limits of existing materials. Ku et all [5] show that Permeselectivity is another important characteristic of a film or tube wall giving the relative barrier properties of different permeants. This selectivity is expressed as a ratio of permeabilities.

$$\alpha_{A/B} = P_A/P_B = S_A/S_B \times D_A/D_B \quad (5)$$

They also show how inorganic fillers (talc, TiO₂, calcium Carbonate, etc) that reduce the free volume of the total system and increasing the torturous diffusion path will decrease permeation rates. Large particles adversely affect desirable mechanical properties. Nano composites however allow for lower amounts of additives with less impact on required functional properties. Surface treatments are also options to explore for improved barrier properties. Tomorrow's tubing designer will have to incorporate all available options.

The above mentioned materials can be combined to optimize barrier properties, flexibility, fitting retention (OD or ID).

Some layer construction options are

AB
ABC
ABCBA
ABCB

An AB construction could be a combination of an Ultra low Density polyethylene, linear low density polyethylene or Ethylene Vinyl Acetate as an out side jacket material comprising a majority of the wall thickness for flexibility with a High density polyethylene layer to improve upon its barrier with HDPE having a very low MVTR. No tie layer is required as the materials are compatible and will combine in the melt stage.

An ABC construction could be a combination a good air barrier material, a good moisture barrier material and a tie layer, when necessary.

An ABCBA construction could incorporate a chemically resistant polyethylene moisture barrier A layer, tie layer B and an EVOH, PVOH air barrier C repeating the tie layer and polyethylene B and A layers..

For increased flexibility, the outside layer can have a lower flex modulus olefin substituted for a more rigid higher density polyethylene becoming an ABCBD construction.

All density groups of polyethylene or copolymer or octane or hexane based LLDPE groups are not created equal related to stress crack and flexing resistance. Higher molecular weight grades with good stress crack resistance must be considered.

Fitting design and long term sealing characteristics require creep properties to be understood.

Process

A good tube design incorporates all aspects of application needs including design for manufacturability.

The process may consist of multiple extruders (2,3,4,5), multiple layer tooling of either manifold distribution or spiral distribution flow technology, initial sizing systems that address tacky out side skin attributes, vacuum controlled sizing chamber, precise water temperature control, laser detection of the outside diameter coupled with flaw detection, consistent pumping and pulling with vector motor driven extruders and belt pullers, cutting system integrated with the puller for exact length control. Feedback control loops will address long term dimensional drift. Processing multiple layers and achieving consistent concentric layers with well bonded interfaces requires state of the art controls, drives, extruders and tooling.

Tooling can be obtained to achieve $\pm 5\%$ on the wall concentricity in either older spill over manifold designs or newer spiral designs. Maintenance of tools is critical, keeping spill over manifold and spiral clearances at design specifications will insure concentric wall layers.

Motor drives should be Vector drives (having evolved from DC and servo). Consistent pumping of all extruders is crucial to thickness, concentricity and diameter control requiring exact temperature and motor speed control. Temperature Controllers should be microprocessor with better than $\pm 1^\circ\text{F}$ control.

Water bath temperature control, consistency of flow and minimal turbulence will allow for consistent sizing and shrinkage control.

[2]

Table 1			
Coefficients of Diffusion and Permeability for Various Gases in Low Density Polyethylene at 25°C			
Gas	Molecular Weight of Gas	Coefficient of	
		Diffusion, $D \times 10^7$ (cm ² sec ⁻¹)	Permeability, $P \times 10^7$ (cc(stp) sec atm) ⁻¹ (cm)
Helium	4	77	0.43
Nitrogen	28	2.9	0.078
Methane	16	1.8	0.28
Propane	44	0.26	0.69

Table 2

MATERIALS	PERMEABILITY			FLEXURAL MODULUS
	H ₂ O (1)	N ₂ (2)	O ₂ (2)	
FEP	0.221	323	715	90,000
PFA	0.33	300	1,000	100,000
ETFE (DuPont TEFZEL 200)	1.4	50	184	150,000
ETFE (FLEX DuPont 2129)				65,000
ETFE (FLEX DAIKIN 610)				120,000
ECTFE HALAR 300	0.45	20	36	240,000
PVDF 760	2.5		3.4	250,000
PVDF (FLEX 2750)				55,000
PVDF (FLEX 2800)				100,000
PCTFE ALLIED SIGNAL	0.027	2.5	12	150,000
ACLON 3000 COPOLYMER				
PCTFE DAIKIN M300P homopolymer	0.016	1	3.3	200,000
THV (3M)	2		225	30,000
EVOH (100% RH)	1.4-3.8		0.065-1.15	600,000
NYLON 6				375,000
NYLON 66 (50% RH)				185,000
NYLON 66 (100% RH)	22		2.6	
NYLON 12	8	0.7	2	190,000
NYLON 12 (FLEXIBLE)				55,000
NYLON (AMORPHOUS/CLEAR)	1.4		5	250,000
POLYETHYLENE (HDPE, Density, 0.960)	0.35	50	65-150	180,000-200,000
POLYETHYLENE (MD, Density, 0.935)	0.75	150	300	78,000
POLYETHYLENE (LDPE, Density, 0.920)	1.25	200	420	50,000
POLYETHYLENE (LLDPE, Density, 0.920)	1.4	200	500	50,000
TPR (PP/Santoprene) 85A durometer				approx. 10,000
POLYETHYLENE TEREPHTHALATE	1.8-3		4.8-9	225,000
POLYESTER ELASTOMER (HYTREL)				10,000 -- 70,000
ULTRALOW DENSITY ETHYLENE OCTENE	2		800	2,500 to 15,000
COPOLYMER (DOW ATTANE/ENGAGE)				
8-10% EVA/POLYETHYLENE	0.33		1161	
POLYPROPYLENE (HOMOPOLY)	0.5-7		150-240	250,000
POLYPROPYLENE (COPOLY)				150,000
POLYPROPYLENE (TPE/Montell Hifax CA10)				13,000 through 190,000
Metallized (aluminum) POLYPROPYLENE (BIAx)	.05-.4		4-6	
PVDC (DOW SARAN)	0.02-.2		0.02-0.8	80,000
Cyclic Olefin Copolymer	0.075		180	500,000
Butyl (Exxon Butyl 268)		60		
EPDM	0.152		4445	
Nitrile Rubber 38% acrylonitrile		39		
Silicone Rubber	6.4		50000	

* (1) grams - mil/100 in 2 24 hrs 100 F° 100% RH
 (2) cc*mil/100 in 2 * day-atm @ 23 C

Compilation of Published Materials Property Data with
 Wall thickness Discounted, Use as Reference Only

Table 3 [6]

Film Material	Oxygen Transmission Rate, 23 C, 0% RH		Film Material	Water Vapor Transmission Rate, 38 C, 90% RH	
	cm ³ um/m ² day	cm ² mm/m ² day atm		g um/m ² day	g mm/m ² day
PVOH	2.5	0.0025325	PVDC	10	0.01
EVOH	4-60	.0041-0.0608	PCTFE	15	0.015
PVDC	15-250	0.0152-0.2533	Polypropylene, Oriented	160	0.16
Nylon MXD6 Oriented	52	0.0527	Polypropylene	260	0.26
Nylon MXD6	250	0.2533	PET Oriented	800	0.8
High Nitril Resins	300	0.3039	PVC rigid	880	0.88
Cellophane	440	0.44572	Nylon MXD6 Oriented	1100	1.1
PET Oriented	1600	1.6208	EVOH	1300	1.3
Nylon 66	2000	2.026	Nylon 66	1500	1.5
Nylon 6	2000	2.026	High Nitril Resins	1600	1.6
PVC rigid	3100	3.1403	Nylon MXD6	2000	2
PCTFE	4400	4.4572	Nylon 6	4300	4.3
Polypropylene, Oriented	44000	44.572	Cellophane	137000	137
Polypropylene	81000	82.053	PVOH	750000	750

Reference: Food Contact Polymeric Materials, review report (ISSN:0889-3144)- Technology LTD., 1992

References;

- [1] Permeability And Other Film Properties Of Plastics And Elastomers, Introduction, vi, Plastics Design Library 1995,
- [2] M. L. Miller, The Structure of Polymers, Polymer Science and Engineering, Reinhold, page 546. (1966).
- [3] Permeability And Other Film Properties Of Plastics And Elastomers, Introduction, iv, Plastics Design Library 1995,
- [4] Melvin Kohan, Nylon Plastics, SPE, Wiley Interscience, p 157 (1973)
- [5] Bon-Cheol Ku; Alexandre Blumstein; Jayant Kumar; Lynne A. Samuelson; Dong Wook Kim, Barrier Properties of Ordered

Multilayer Polymer Nanocomposites, Dekker Encyclopedia of Nanoscience and Nanotechnology (2004)

- [6] J.A. Sidwell, Food Contract Polymeric Materials, Rapra Review Reports, Vol.6, No. 1, 61, 1992

Author Biography

Don Curran is a graduate of Drexel University with a BS degree in Metallurgical Engineering, 1974. He has worked in the plastics industry for 33 years with Dupont and Saint-Gobain Performance Plastics. His work with and knowledge of Fluoropolymers and Engineering polymers and processes has helped him successfully develop many products and programs for numerous major world known corporations and applications.