SAND2013-7641P

Exceptional service in the national interest

Sandia National Laboratories

Technical Document on Polymers for Hydrogen Infrastructure

Rachel Barth[1] and Kevin Simmons[2]

September 12, 2013

[1]SNL, [2]PNNL

U.S. DEPARTMENT OF ENERGY

NNSA

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND No XXXX-XXXXX

Introduction

- We receive continued requests for information on polymers similar to Technical Reference for metals

- We are compiling a document on properties of polymers used in hydrogen vehicles and delivery infrastructure
  - Relevant applications and materials
  - Technical data
  - Gap analysis

Differences between polymers and metals in the context of hydrogen compatibility

- Framework for metals is well developed
  - ASTM specification of materials
  - Agreement on property definitions
  - Hydrogen compatibility of metals: Technical Reference
- Polymers are different
  - Not subject to hydrogen embrittlement in the same ways
  - Affected by hydrostatic pressure
  - Viscoelastic behavior
    - Temperature dependencies, e.g. glassy/rubbery transitions
    - Rate dependencies

Properties are highly dependent on molecular weight, processing history

Structure of Document

- Section 1: Applications and Materials
  - Fueling station
  - On board vehicle
  - Pipelines
- Section 2: Technical Data
  - Materials properties
    - Pressure effects (up to 100 MPa)
    - Temperature effects
      - gaseous H_2: −40°C to 85°C
      - liquid H_2: ~20K
      - hot seals in compressors: up to 200°C
  - Hydrogen effects
    - Gas transport properties (permeability, diffusivity, solubility)
    - Decompression effects
  - Test methods
- Section 3: Gap Analysis

Scope

- Within scope
  - Polymer properties at relevant operating temperatures/pressures
    - Not structures (e.g., pipes or pressure vessels)
    - Constituents of multicomponent systems only
  - Published, peer-reviewed data
- Out of scope
  - Fuel cell components (e.g., membranes)
  - Polymers for solid state hydrogen storage
  - Experimental (non-standard) copolymers, blends, treatments, processing conditions
- Excluded for lack of evidence
  - Chemical reactions between polymer and hydrogen
  - Effects of impurities (CO, CO_2, O_2, H_2O in gas; agents in the polymer)

Materials for hydrogen components

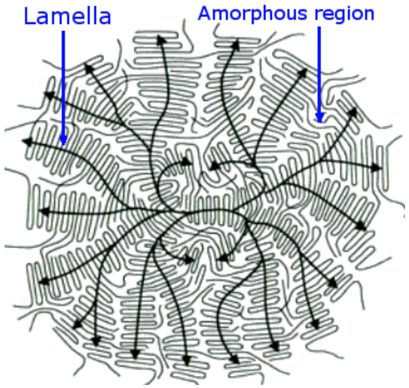
ion Materials for Hydrogen
onents

Material Type	Check Valves	Control Valves	Tanks and Pipes
Viton	x	x	
Buna-N	x	x	
Teflon	x	x	
EPR	x	x	
Fluorosilicone	x		
Silicone	x		
Neoprene	x		
PEEK	x	x	
PEEK	x	x	
Nylatron		x	
Vespel		x	
PCTFE		x	
Epoxy			x
Fiberglass			x
Carbon Fiber			x
HDPE			x

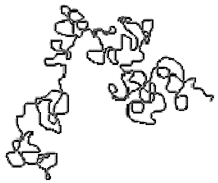
, PNNL 509-375-3651, kevin.simmons@pnnl.gov

Categories of materials

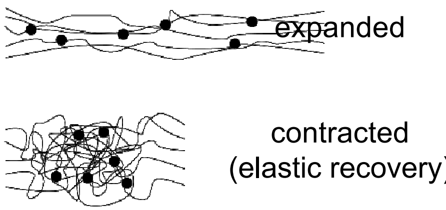
- Thermoplastics
  - Semicrystalline (e.g., HDPE, PTFE)
    - Liners
    - Valve seats
    - Seals
  - Amorphous (e.g., PVC, CPVC)
    - Low-pressure applications
- Crosslinked polymers
  - Elastomers
    - O-rings
    - Seals
    - Hoses
  - Epoxies
    - Containment



Semicrystalline polymer spherulite (Wikipedia, *Crystallization of polymers*)



Amorphous coil http://www.pslc.ws/macrog/ps5.htm



(Wikipedia, *Elastomer*)

Organization of technical data section

- Introductory matter
- For each property of interest:
  - Description and definitions
  - Applicable ASTM specifications
  - Review of existing literature
  - Data (separately for each polymer category)

Table 3.1 Smooth tensile properties of semicrystalline polymers under hydrostatic pressure

Material	Description	Strain rate (min^{-1})	Pressure medium	Pressure (MPa)	Tensile strength[a] (MPa)	Elongation at max stress (%)	Modulus of elasticity (MPa)	Ref.
HDPE	ρ=0.946	0.20	kerosene	0.1 69 140 210 280	26.1 40.1 48.1 51.7	14 12 5.4	1200 1800 2400 3000 3200	[8]
HDPE	ρ=0.950	0.04	castor oil + 20% methanol	0.1 140 280	25 34 55	15 14 9.2	1100 2000 2700	[7]
HDPE	ρ=0.96	0.30 0.14	castor oil	0.1 770	32 92			[2]
PA 6,6	cold drawn	0.14	silicone fluid MS200	0.1 200	51 72			[2]
PA11	α=22% (Arkema)	0.52	air, 26°C N_2, 26°C H_2, 26.5°C	0.1 3 3	29.8 31.1 27.8		730 780 700	[9]
PTFE		0.20	kerosene	0.1 210 410	17[b] 47[b] 62[b]	130 60 27		[10]
PTFE	Halon G-80 ρ=2.17 α~57%	0.26	water	0.1 280 550 830	13.6 61.7[b] 79.7[b] 96.5[b]	80 110 65 63		[3]

[a]Strength at yield unless otherwise indicated.

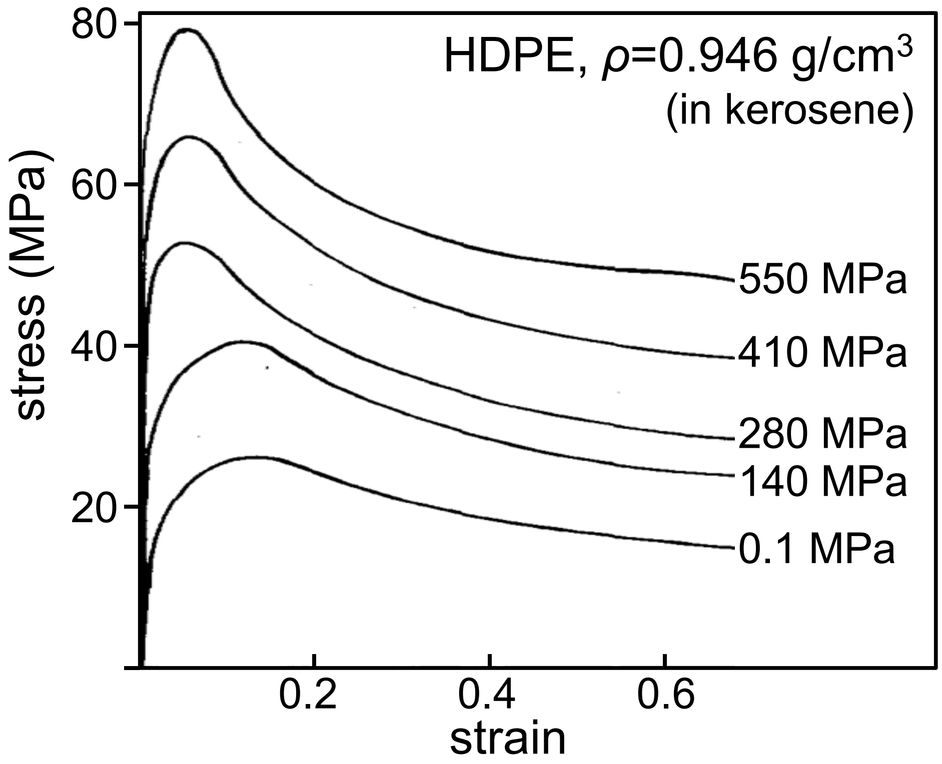
Example data and trends

- Glass transition temperature
  - Affects amorphous fraction
  - Generally, increases with pressure
  - However, certain pressure media may reduce T_g (we don't know about H_2)

Elastomer	T_g, °C (1 atm, 1 Hz)	Shift, °C per 100 MPa	Ref.
Natural rubber	-50	24	[1]
	-50	29	[2]
	-50	16	[3]
Silicone rubber	-50	16	[3]
Fluorosilicone rubber	-50	16	[3]

Tensile behavior under high hydrostatic pressure

- Little to no data available in gaseous hydrogen

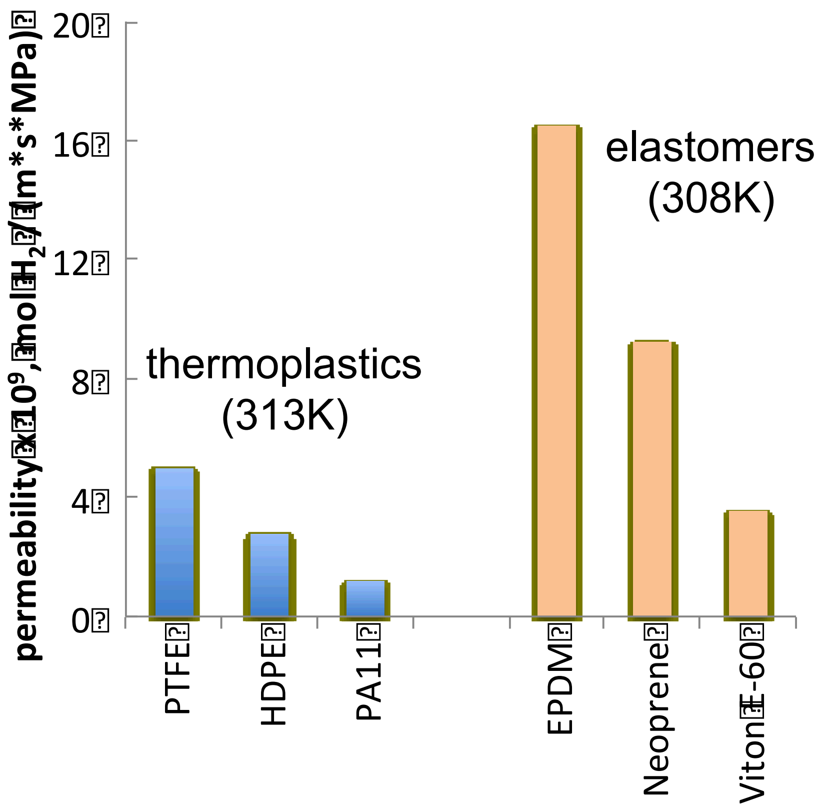


Mears et al., *J. Appl. Phys.* 40, 4229 (1969)

- Trends
  - Tensile strength at yield increases with pressure

Hydrogen permeability

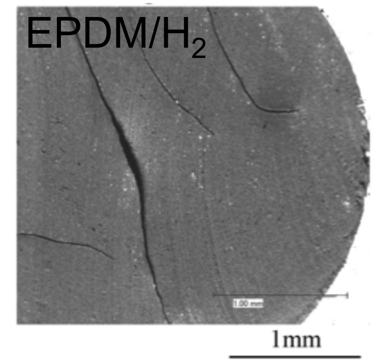
- Arrhenius temperature dependence

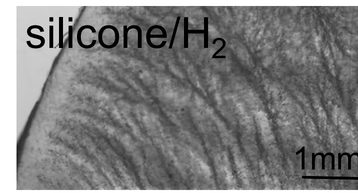


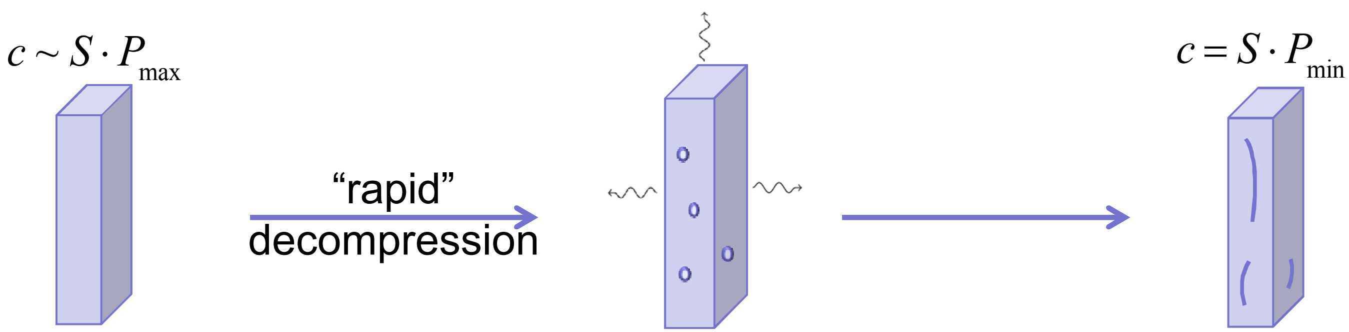
Rapid gas decompression

- A small dataset exists, primarily for elastomers
  - Mostly CO_2, N_2, Ar
  - Two groups have published work with H_2
  - Test methods are rarely directly comparable

- Strong dependence on temperature, decompression rate, gas solubility and diffusivity, material strength







bubble nucleation/growth and gas escape (diffusion controlled) *[reversible]*

blistering/cracking (surface tension > local material failure criterion) *[irreversible]*

Gaps

- Fundamental
  - Polymer-H_2 interactions largely unexplored at P > 10 MPa
    - Plasticization? Degradation?
      - Neither of the above expected to be significant, but this has not been shown
    - Pressure effect on H_2 solubility, permeability

- Incomplete characterization of materials of interest
  - Durability
  - Long-term physical and chemical compatibility of trace contaminants
    - Fuel additives, agents in polymer
  - Permeation coefficient units

- Large amounts of unpublished data exist

- Test methods
  - Decompression testing inconsistent

Gap analysis

- Organization of gaps