

Technical Reference on Hydrogen Compatibility of Materials

Nonmetals:
Polymers (code 8100)

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1. General

Polymers are a diverse category of materials characterized by chains of covalently-bonded atoms with repeating structural units. The materials can be processed in numerous ways with almost infinite variation. The properties of polymers are determined by a number of factors including crystallinity, density, chain orientation, cross-linking, purity, phase distribution, etc.

We are unaware of hydrogen compatibility studies for common polymer materials that might be expected in gaseous hydrogen service, thus we have eliminated the sections on mechanical properties and microstructural considerations. Gas permeation through polymer materials, however, has been extensively studied; therefore we provide a non-exhaustive summary of hydrogen transport data in common polymer materials.

Relatively large amounts of hydrogen are often soluble in polymer materials; therefore, exposure to high-pressure hydrogen may cause damage (blistering or swelling) of the polymer materials. This is manifest in high-pressure applications due to depressurization of a system (or rapid temperature changes) as hydrogen expands in free volume and at interfaces within the polymers. .

1.1 Composition and microstructure

Polymers are generally characterized by the composition and molecular structure of the material. Nomenclature often evolves from common usage and generally does not incorporate structural details. We use ASTM D1418 and D1600 for guidance on naming. Table 1.1.1 includes the abbreviations used in this document.

2. Permeability, Diffusivity and Solubility

Hydrogen transport in polymers has been extensively studied, particularly for high-vacuum systems. Similar to studies of metals, studies of the hydrogen permeation in polymers have generally been performed at low pressure. Permeability, diffusivity and solubility are often assumed to be independent of pressure for metals and data generated at low-pressure are extrapolated to describe high-pressure systems. This extrapolation implies that hydrogen transport and solubility properties are independent of concentration (i.e., Fickian diffusion). While concentration-dependent transport properties (non-Fickian diffusion) are often observed in polymers, we are unaware of any studies on polymers that suggest hydrogen transport and solubility are dependent on concentration. Thus, until studies show otherwise, we assume that hydrogen permeability, diffusivity and solubility in polymers are independent of pressure. Unlike metals, hydrogen transport in polymer materials is sufficiently rapid that the permeation rates can generally be measured at or near ambient temperature.

The permeability (Φ) is determined from Fick's first law for diffusion, and represents a steady-state property of the material (assuming diffusion is independent of pressure). It is defined in the same way as for metals, such that

$$\Phi = DS \quad (1)$$

where D is the diffusivity and S is the solubility. Hydrogen transport in polymers differs from metals in one important aspect: hydrogen does not dissociate prior to dissolution in the material, thus the concentration of hydrogen dissolved in the polymer (c) is proportional to the fugacity (f , which equals the pressure in the limit of an ideal gas):

$$S = c/f \quad (2)$$

while in metals c is proportional to \sqrt{f} . In materials where hydrogen does not dissociate, such as polymers, it should be clear from equations 1 and 2 that the units of permeability are

$$[\Phi] = [\text{diffusivity}] \frac{[\text{concentration}]}{[\text{pressure}]} = \frac{\text{m}^2}{\text{s}} \frac{\text{mole H}_2/\text{m}^3}{\text{MPa}} = \frac{\text{mole H}_2}{\text{m} \cdot \text{s} \cdot \text{MPa}} \quad (3)$$

Other forms of these units are, of course, possible and they can be a significant source of confusion. The units in equation 3 are commonly accepted for high-pressure hydrogen since they do not require definition of a reference state.

In tables 2.1 through 2.4, the hydrogen transport properties for a number of polymeric materials are summarized. A secondary resource [1] is used for these values and no effort was made to verify the primary references; the interested reader is also referred to Ref. [2], which contains a lists of primary sources by material. A selection of the hydrogen transport data from Ref. [1] is summarized here. Table 2.1 provides hydrogen transport properties for several common categories of plastics at approximately room temperature. Table 2.2 provides the transport properties for several commercial elastomers near room temperature, while Table 2.3 provides properties for a number of elastomers (rubbers) from a range of classes at room temperature and, when available, at elevated temperature.

Permeability, diffusivity and solubility follow a classic exponential form:

$$A = A_0 \exp\left(\frac{-E_A}{RT}\right) \quad (4)$$

where A_0 and E_A are material-dependent constants, R is the universal gas constant ($8.31447 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is temperature in Kelvin. Table 2.4 provides the constants from equation 4 that summarize the temperature dependence of these properties for several of the materials from the previous tables. The temperature dependence of hydrogen transport and solubility for the materials in Table 2.4 is plotted in Figure 2.1 (permeability), Figure 2.2 (diffusivity) and Figure 2.3 (solubility); these properties are linear when plotted on a log scale as a function of $1/T$ as shown in these figures.

3. References

1. S Pauly. Permeability and Diffusion Data. in: J Brandrup, EH Immergut and EA Grulke, editors. Polymer Handbook, fourth edition. New York: John Wiley and Sons (1999).
2. SA Stern, B Krishnakumar and SM Nadakatti. Permeability of Polymers to Gases and Vapors. in: JE Mark, editor. Physical Properties of Polymers Handbook. Woodbury NY: American Institute of Physics (1996).

Table 1.1.1. Standard abbreviations (from ASTM D1418 and D1600) for common polymeric materials reported in this document.

Abbreviation	Term (AISI/ASTM)
<i>Plastics</i>	
LDPE	Low density polyethylene plastics
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluorethylene
PVC	Poly(vinyl chloride)
PVF	Poly(vinyl fluoride)
<i>Rubbers (Elastomeric Polymers)</i>	
CIIR	Chloro-isobutene-isoprene rubber
CR	Chloroprene rubber
IIR	Isobutene-isoprene rubber
NR	Natural rubber
NBR	Acrylonitrile-butadiene rubber
NIR	Acrylonitrile-isoprene rubber
SBR	Styrene-butadiene rubber
CSM	Chloro-sulfonyl-polyethylene
EPDM	Terpolymer of ethylene, propylene, and a diene
FKM	One type of fluoro rubber
VMQ	Silicone rubber (vinyl and methyl substituents)

Table 2.1. Hydrogen transport properties for some common plastics from Ref. [1]; abbreviations from Table 1.1.1. Values in parenthesis are not given in Ref. [1], and were calculated using equation 1.

Material	Temperature (K)	$\Phi \times 10^9$ $\left(\frac{\text{mol H}_2}{\text{m} \cdot \text{s} \cdot \text{MPa}}\right)$	$D \times 10^{12}$ $\left(\frac{\text{m}^2}{\text{s}}\right)$	S $\left(\frac{\text{mol H}_2}{\text{m}^3 \cdot \text{MPa}}\right)$
LDPE 0.914 g/cm ³	298	3.3	47.4	70.5
PP 0.907 g/cm ³ , 50% crystallinity	293	13.8	210	(65.9)
PS biaxial structure	298	7.58	—	—
PMMA	308	1.24	—	—
PVC unplasticized	298	0.58	50	12
	300	0.80	48	(16.7)
PTFE	298	3.3	—	—
	298	3.23	14.7	220
PVF	308	0.18	—	—
PVF (Kynar)	308	0.180	33.6	(5.36)

Table 2.2. Hydrogen transport properties for some common commercial elastomers from Ref. [1].

Material	Temperature (K)	$\Phi \times 10^9$ $\left(\frac{\text{mol H}_2}{\text{m} \cdot \text{s} \cdot \text{MPa}}\right)$	$D \times 10^{12}$ $\left(\frac{\text{m}^2}{\text{s}}\right)$	S $\left(\frac{\text{mol H}_2}{\text{m}^3 \cdot \text{MPa}}\right)$
Hypalon 40 (CSM)	308	3.68	265	14.5
Kraton FG	308	22.4	1160	19.2
Viton GF (FKM)	308	7.32	345	21.0

Table 2.3. Hydrogen transport properties for some common elastomeric polymers from Ref. [1]; abbreviations from Table 1.1.1.

Material	Temperature (K)	$\Phi \times 10^9$ $\left(\frac{\text{mol H}_2}{\text{m} \cdot \text{s} \cdot \text{MPa}}\right)$	$D \times 10^{12}$ $\left(\frac{\text{m}^2}{\text{s}}\right)$	S $\left(\frac{\text{mol H}_2}{\text{m}^3 \cdot \text{MPa}}\right)$
Poly(butadiene) (BR)	298	14.1	960	14.5
CIIR shore 70‡	293	0.857	—	—
	353	11.6	—	—
CR shore 42‡	293	2.23	—	—
	353	27.3	—	—
Neoprene (CR)	308	9.24	933	9.9
Neoprene G (CR)	298	4.55	380	12.8
Poly(isobutene- <i>co</i> -isoprene) (IIR) 98/2	298	2.42	152	15.8
Poly(butadiene- <i>co</i> -acrylonitrile) (NBR) 80/20 (Perbunan†) 61/39 (Hycar†)	298	8.43	643	13.2
	298	2.39	243	9.7
shore 70‡	293	1.45	—	—
	353	12.1	—	—
NBR shore 60‡	293	1.67	—	—
	353	21.1	—	—
shore 50‡	293	2.04	—	—
	353	17.1	—	—
Poly(isoprene- <i>co</i> -acrylonitrile) (NIR) 74/26	298	2.49	247	10.1
NR shore 66‡	293	4.09	—	—
	353	38.4	—	—
SBR shore 52‡	293	2.98	—	—
	353	21.7	—	—
CSM shore 70‡	293	1.31	—	—
	353	9.28	—	—
EPDM shore 68‡	293	6.96	—	—
	353	38.4	—	—
FKM shore 70‡	293	1.51	—	—
	353	18.6	—	—
VMQ shore 50‡	293	100	—	—
	353	260	—	—

† trade names

‡ shore durometer (hardness)

Table 2.4. Relationships for temperature dependence of hydrogen transport properties for some common polymers from Ref. [1]; abbreviations from Table 1.1.1. Values in parenthesis are not given in Ref. [1], and were calculated using equations 1 and 4 with values reported in the other tables.

Material	Temperature Range (K)	Permeability $\Phi = \Phi_o \exp(-H_\Phi / RT)$		Diffusivity $D = D_o \exp(-H_D / RT)$		Solubility, $S = \Phi/D$ $S = S_o \exp(-\Delta H_s / RT)$	
		$\Phi_o \times 10^3$ $\left(\frac{\text{mol H}_2}{\text{m} \cdot \text{s} \cdot \text{MPa}}\right)$	H_Φ $\left(\frac{\text{kJ}}{\text{mol}}\right)$	$D_o \times 10^6$ $\left(\frac{\text{m}^2}{\text{s}}\right)$	H_D $\left(\frac{\text{kJ}}{\text{mol}}\right)$	S_o $\left(\frac{\text{mol H}_2}{\text{m}^3 \cdot \text{MPa}}\right)$	ΔH_s $\left(\frac{\text{kJ}}{\text{mol}}\right)$
PP 0.907 g/cm ³ , 50% crystallinity	293 - 343	99.9	38.5	—	—	—	—
PVC unplasticized	298 - 353	0.651	34.5	(55.7)	34.5	(11.7)	0
PTFE	293 - 403	0.0185	21.4	—	—	—	—
Poly(butadiene) (BR)	298 - 323	0.959	27.6	(5.20)	21.3	(185)	6.3
Neoprene G (CR)	288 - 323	3.93	33.9	(26.2)	27.6	(162)	6.3
Poly(isobutene- <i>co</i> -isoprene) (IIR) 98/2	298 - 323	5.71	36.4	(133)	33.9	(43.4)	2.5
Poly(butadiene- <i>co</i> -acrylonitrile) (NBR) 80/20 (Perbunan†) 61/39 (Hycar†)	298 - 323	1.57	30.1	(23.2)	26.0	(69.1)	4.1
		6.65	36.8	(91.1)	31.8	(72.8)	5.0
Poly(isoprene- <i>co</i> -acrylonitrile) (NIR) 74/26	298 - 323	11.7	38.1	(67.1)	31.0	(178)	7.1

† trade names

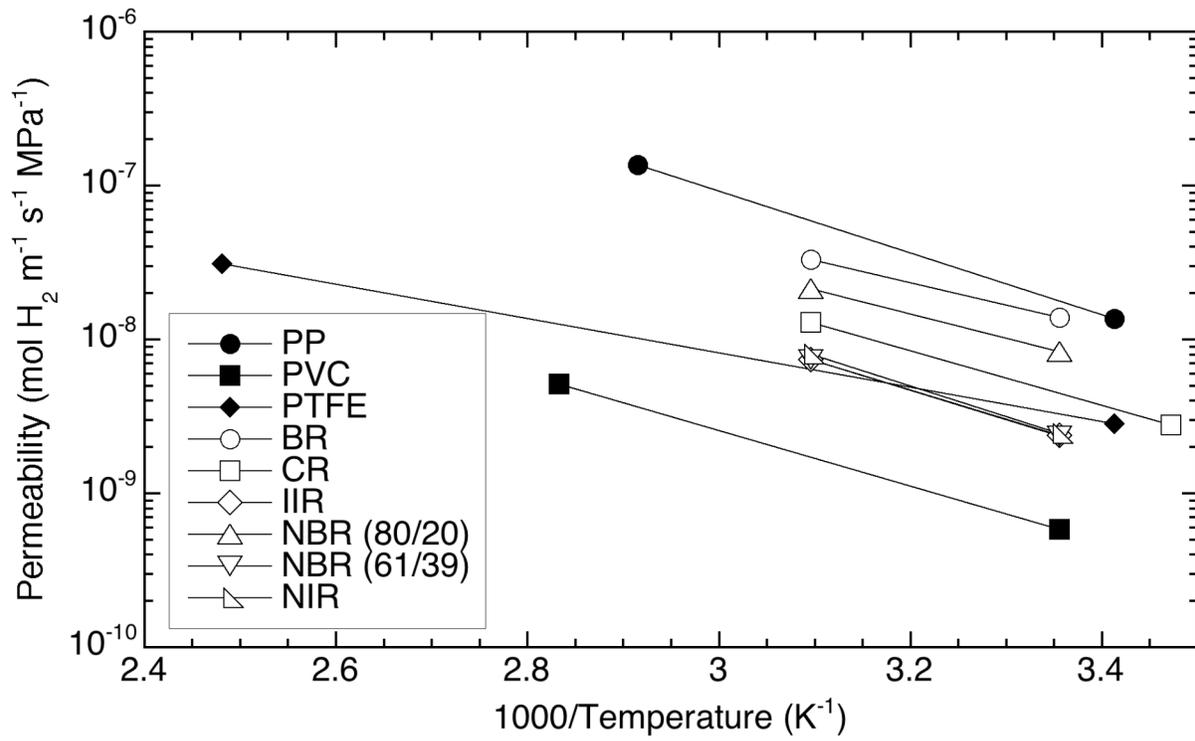


Figure 2.1. Permeability relationships (from Table 2.4) for several polymers.

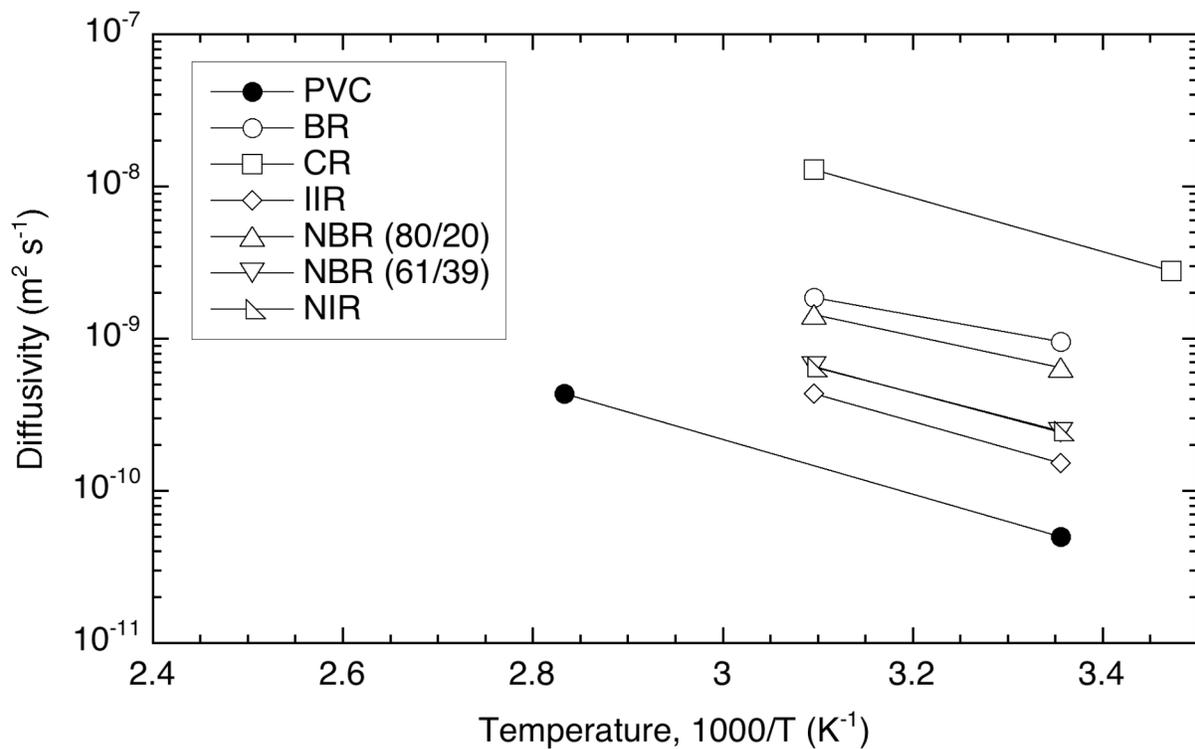


Figure 2.2. Diffusivity relationships (from Table 2.4) for several polymers.

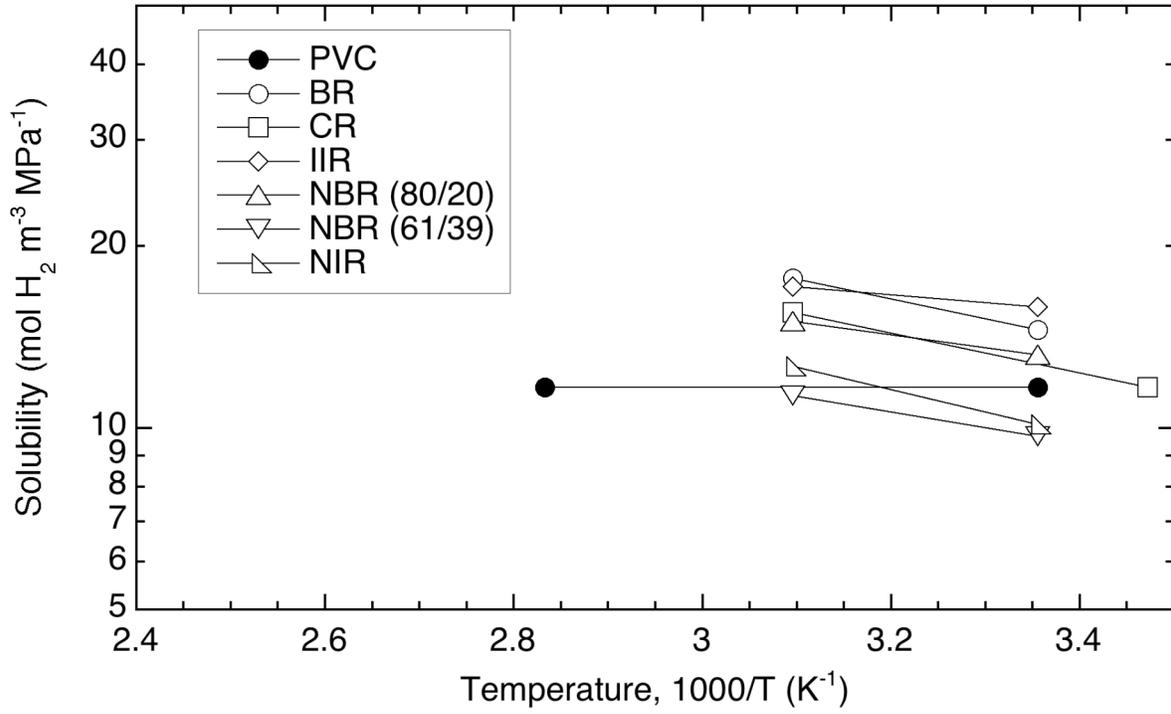


Figure 2.3. Solubility relationships (from Table 2.4) for several polymers.