DuPont™ Formacel®

foam expansion agent

Zero-ODP Blowing Agents for Polyurethane Foams

J. A. Creazzo, H. S. Hammel, P. L. Bartlett—November, 1992

The "Next" Generation

As we move toward final phaseout of chlorofluorocarbon (CFC) blowing agents, new compounds and technologies are emerging to produce the polyurethane foams essential to so many products. Among the new blowing agents being developed, compounds with no ozone depletion potential (ODP) and minimal global warming potential (GWP) are ultimately the most environmentally desirable.

In considering zero-ODP compounds that are currently available, the potential hydrofluorocarbon (HFC) candidates (**Table 1**) are gases at ambient conditions. With the objective to understand feasibility for using low-boiling HFCs as polyurethane foam blowing agents, a study of DuPont™ Formacel® Z-4 (HFC-134a) and Formacel® Z-2 (HFC-152a) was begun. This bulletin summarizes developments in that effort, thus far.

Physical Properties

Table 2 summarizes physical properties of interest for Formacel® Z-4 and Formacel® Z-2. **Figure 1** compares the vapor pressure versus temperature curves for Freon® 11 (CFC-11) and Formacel® S (HCFC-22), Z-2, and Z-4.

An appealing property of these zero-ODP gases is their low molecular weights. Since it is gas volume that expands the foam, a low molecular weight means less pounds of blowing agent are needed for the same gas volume as compared to higher molecular weight compounds.

In considering alternative blowing agents for insulation foams, thermal conductivity of the vapors is important because of its contribution to the foams' insulation value. **Figure 2** shows the vapor thermal conductivity (VTC) of the zero-ODP gases versus temperature. We see that the VTC of Formacel® Z-2 and Z-4 are lower than air, imparting insulation value to the foam. An added advantage of the low-boiling gases is that they will remain a vapor in the foam cells at much lower temperatures than the higher-boiling liquid blowing agents. This effect will improve a foam's insulation value at low operating temperatures.

Table 1
Alternative Blowing Agents Comparing Boiling Points and Environmental Properties

Compound	Boiling Point, °C	Ozone Depletion Potential	Global Warming Potential (GWP) 100 Yr ITH, GWP for CO_2 = 1
HCFC-141b	32.0	0.11	630
HCFC-142b	–9.8	0.065	2,000
Formacel® S	–40.8	0.055	1,700
Formacel® Z-4	–26.1	0	1,300
Formacel® Z-2	–24.7	0	140

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Table 2
Properties of Zero-ODP Alternatives

	Formacel® Z-4	**Formacel® Z-2**
Formula	CH_2FCF_3	CHF_2CH_3
Molecular Weight	102.0	66.0
Boiling Point (°C)	–26.1	–24.2
(°F)	–14.9	–11.5
Vapor Pressure @ 25°C (77°F)		
psig	82	72
bars	6.7	6.0
Ozone Depletion Potential	0	0
Global Warming Potential (GWP)		
100 Yr. ITH, GWP for CO_2 = 1	1,300	140
Vapor thermal Conductivity at 140°F		
Btu/hr•ft °F	0.0102	0.0105
mW/m•K	17.7	18.2
Flammability Limits in Air (vol %)	None	3.9–16.9
Latent Heat of Vaporization at B.P.		
Btu/lb	93.4	141.5
kJ/Kg	217.1	328.9
Liquid Density at 25°C (77°F)		
lb/ft^3	75.3	56.1
gm/cc	1.206	0.898
Toxicity	1,000 ppm (AEL)	1,000 ppm (AEL)

AEL = DuPont Acceptable Exposure Limit

Vapor Pressure and Solubility Data

One of the first considerations in using an HFC gas in polyurethane (PUR) and polyisocyanurate (PIR) foams is evaluating its compatibility with the foam system polyols. This evaluation is underway for Formacel® Z-4; equivalent experiments with Formacel® Z-2 will follow later. Data is being developed for two parameters: HFC solubility in polyols, and vapor pressure versus temperature for HFC/polyol mixtures.

Initial Formacel® Z-4 experiments have shown that HFC solubility in the polyols is limited. When that solubility limit is exceeded, the HFC/polyol mixture can either form an emulsion or separate into two phases. The blowing agent solubility limit depends on the polyol; the Formacel® Z-4 data (**Table 3**) shows greater blowing agent attraction for polyether polyols than for polyester polyols.

Table 3
Formacel® Z-4 Compatibility with Foam Polyols

Polyol Type	**Wt % Range for Single-Phase Mixture from 10°C to 50°C**
Aromatic Amine Polyethers	0–10
Mannich-Type Polyethers	10–20
Sucrose/Sucrose-amine Polyethers	20–50+
Polyesters	5–30

Note: The compatibility range for single-phase mixtures does not necessarily mean complete blowing agent solubility; in some cases, stable emulsions result.

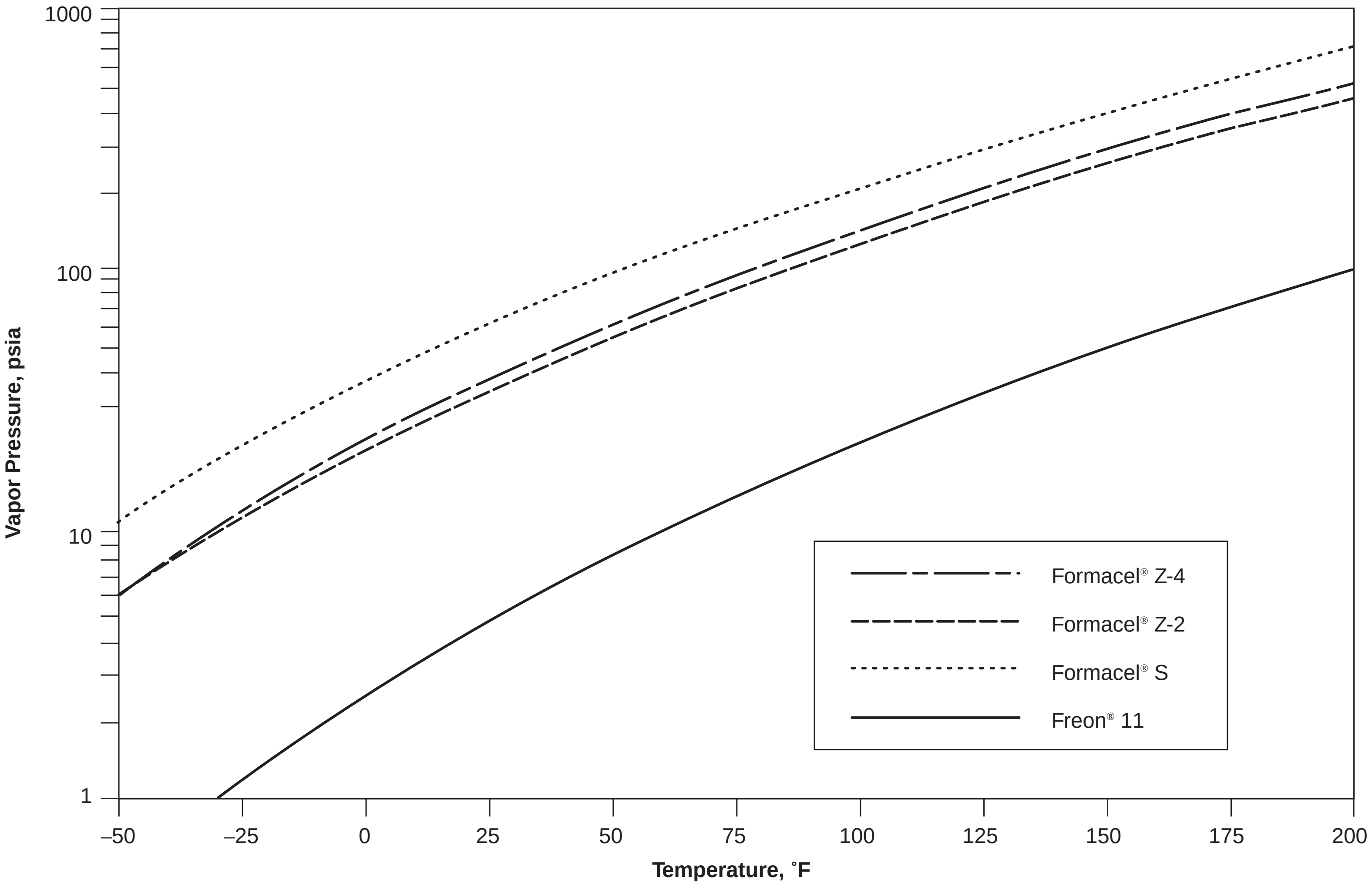


Figure 1. Formacel® Blowing Agents' Vapor Pressure

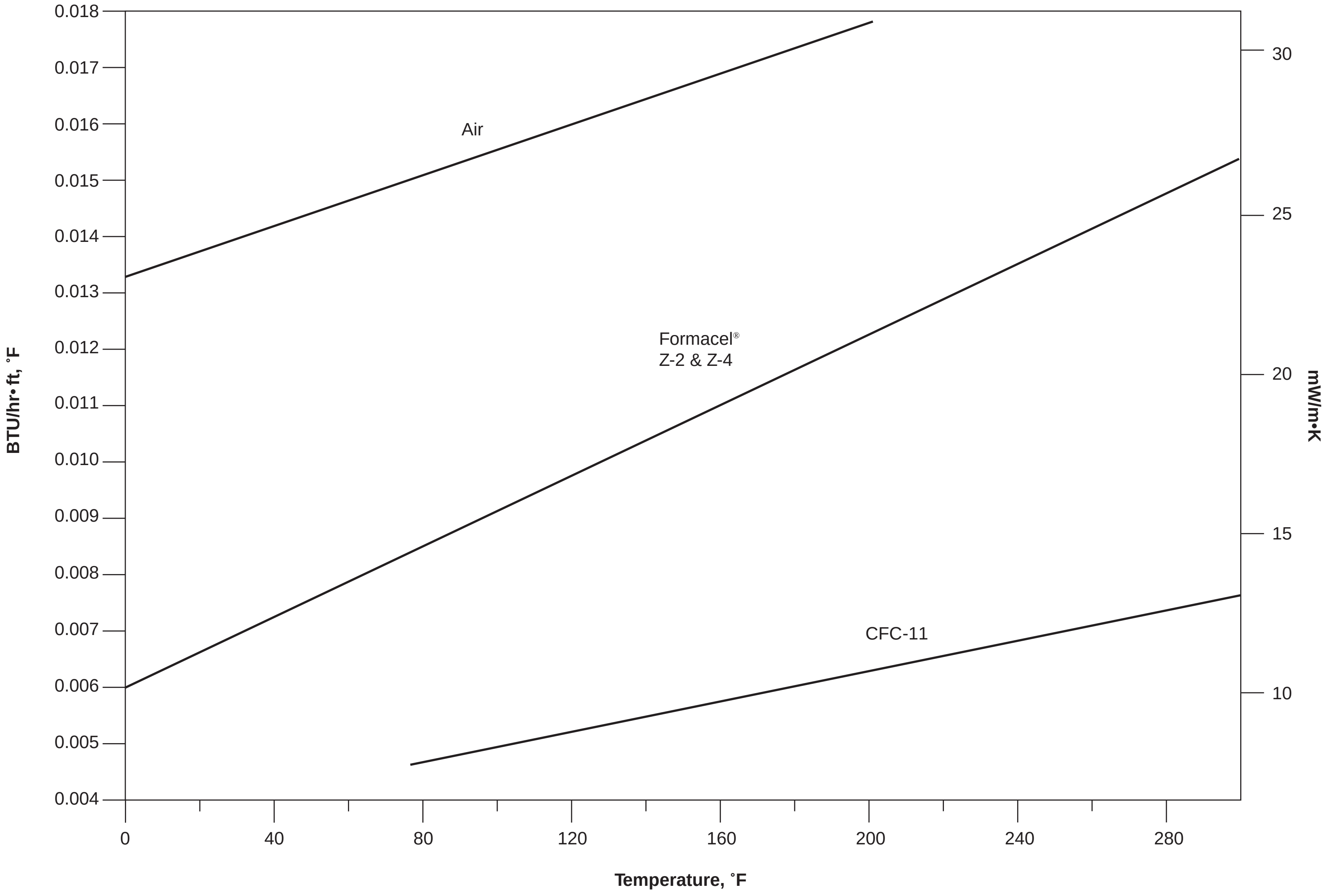


Figure 2. Vapor Thermal Conductivities

Vapor pressure of the Formacel® Z-4/polyol mixtures were also measured during the solubility experiments. The measurements were made at three temperatures, and typical pressures for different Formacel® Z-4 concentrations are plotted in **Figures 3** and **4**. Polyester polyol data is plotted in **Figure 3**, and polyether polyol data is plotted in **Figure 4**; the differences in affinity results in different B-side vapor pressures. For the polyether polyols, **Figures 4A, 4B,** and **4C** show the effect on vapor pressure for different Formacel® Z-4 affinity. In **Figure 4B**, for example, we see that vapor pressure will increase gradually with Formacel® Z-4 concentration when Z-4 affinity for the polyol is high; conversely, when affinity is low, vapor pressures increase more quickly at lower Z-4 concentrations.

There are potential chemical and mechanical means available to increase HFC solubility in the polyols. Chemically, for example, surfactants can increase solubility, and mechanically, high energy or very high pressure mixing could help. Both of these areas are being explored, and will be discussed in future bulletins.

Viscosity

One important function served by the blowing agent is to reduce the B-side viscosity to levels within the pumping capabilities of the processing equipment. Formacel® Z-2 and Z4 accomplish this as well as Freon® 11. This has been observed qualitatively in the solubility/vapor pressure experiments.

The fluorochemicals Laboratory, however, has the capability for measuring solution viscosities under pressure. These experiments are underway for several different polyols; the first set of results are plotted in **Figure 5**. Additional data will be reported in future bulletins.

Materials Compatibility

For any new blowing agent, it is important to assess effects on elastomer and plastic materials of construction. Simple exposure of different materials to the blowing agent provides insight into their compatibility. In compatibility tests, linear swell and % extractables are measured after exposure. The amount of linear swell is a valuable guide in determining whether or not the elastomer or plastic is suitable for use. The % extractables is a measure of the coupon's weight loss from exposure.

When foaming with high-boiling liquids, there is a greater potential for contacting materials of construction with liquid blowing agent. With low-boiling blowing agents, materials of construction in foamed products are more likely to contact only blowing agent vapors. Compatibility tests were done for Formacel® Z-2 and Z-4, in which coupons were exposed to both liquid and vapor blowing agent samples.

Table 4 shows a list of the elastomers and plastics tested; **Table 5** provides a broad summary of results. These simple exposure tests help screen effects on materials of construction. As always, final materials selection should include testing more specific to the application.

Chemical Stability

As with other alternatives, the stability of Formacel® Z-2 and Z-4 in B-side systems and foams must be considered; this stability is being studied for different type B-side systems and foams.

The first tests evaluated Formacel® Z-2 and Formacel® Z-4 stability in a sucrose-amine polyether polyol with an amine catalyst, a potassium catalyst, a tin catalyst, or an amine catalyst neutralized with an organic acid. The initial results including analysis of the volatile components, indicate that there is no degradation of Formacel® Z-2 and Z-4 in any of the systems, even at elevated temperatures. The results are summarized in **Table 6**.

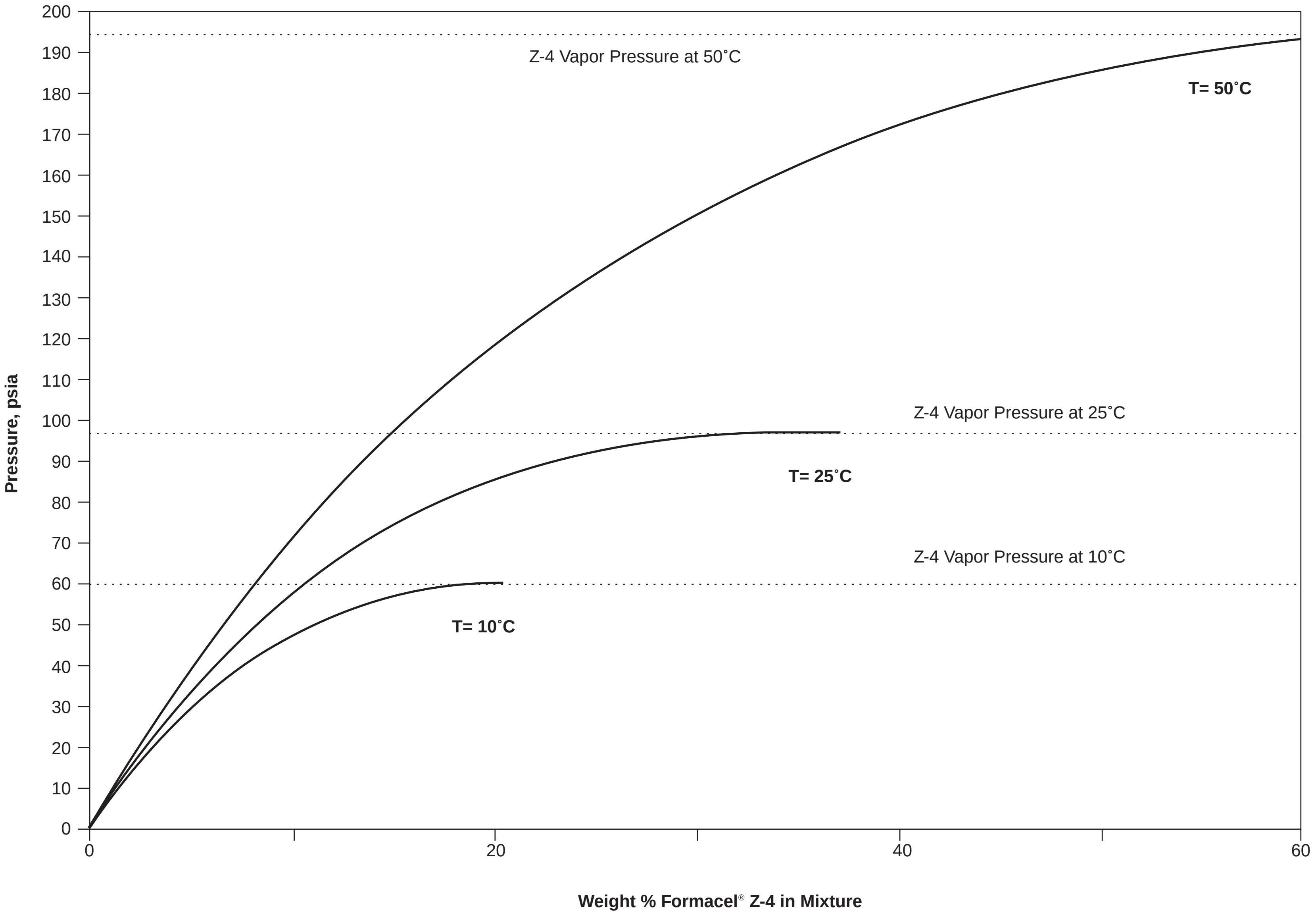
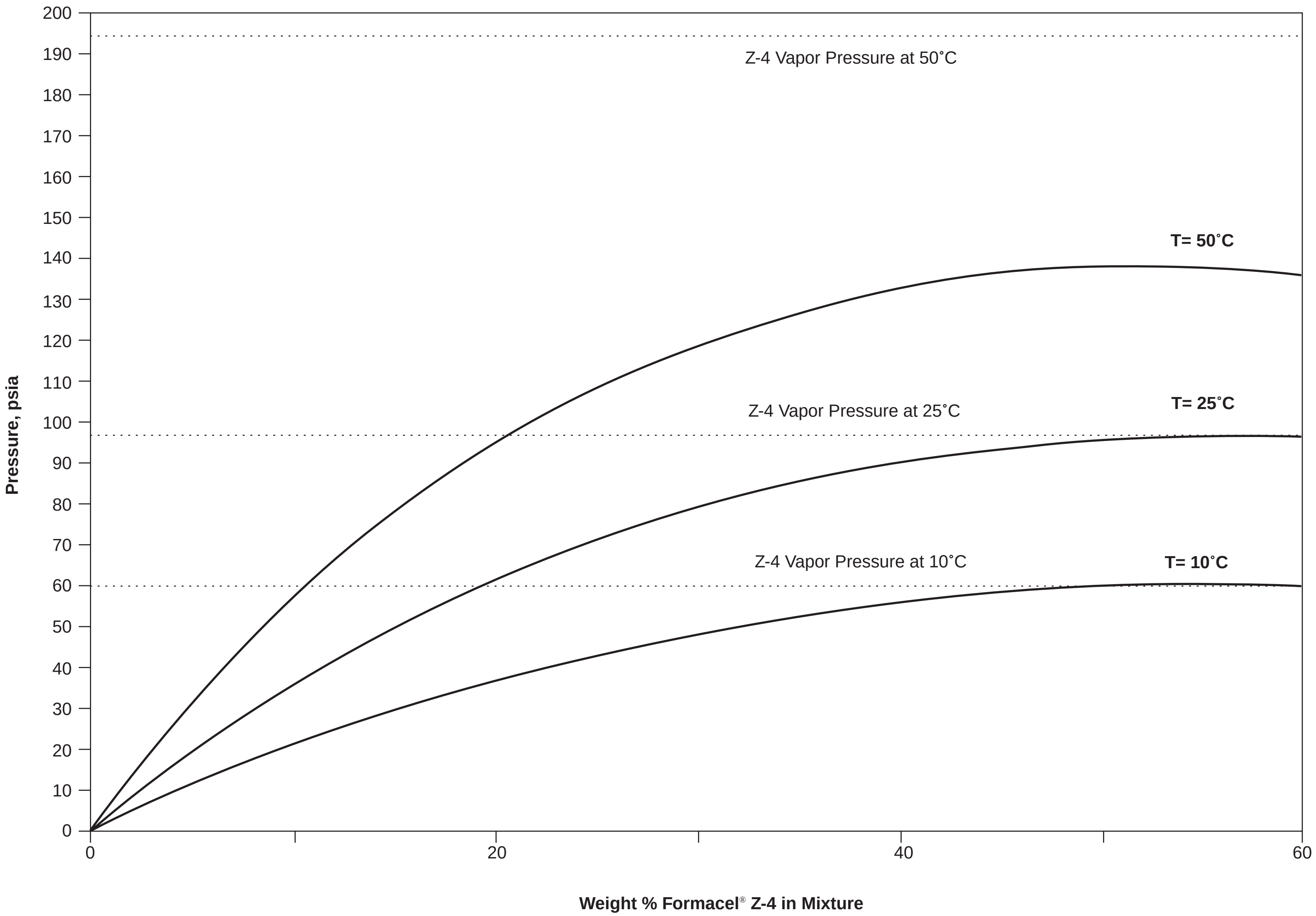


Figure 3. Formacel® Z-4 in Polyester Polyols

Figure 4. Formacel® Z-4 in Polyether Polyols



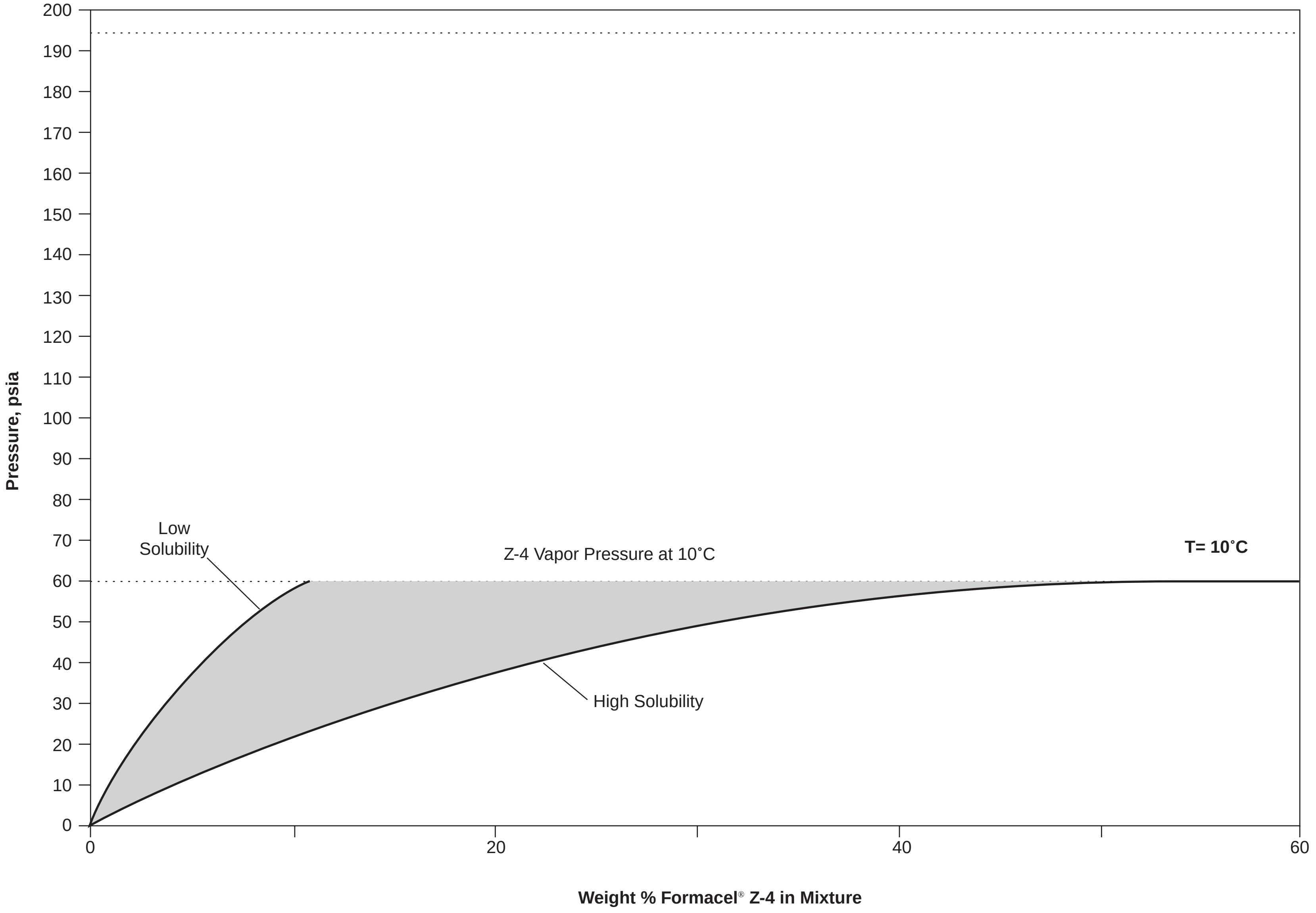


Figure 4A. Formacel® Z-4 in Polyether Polyols

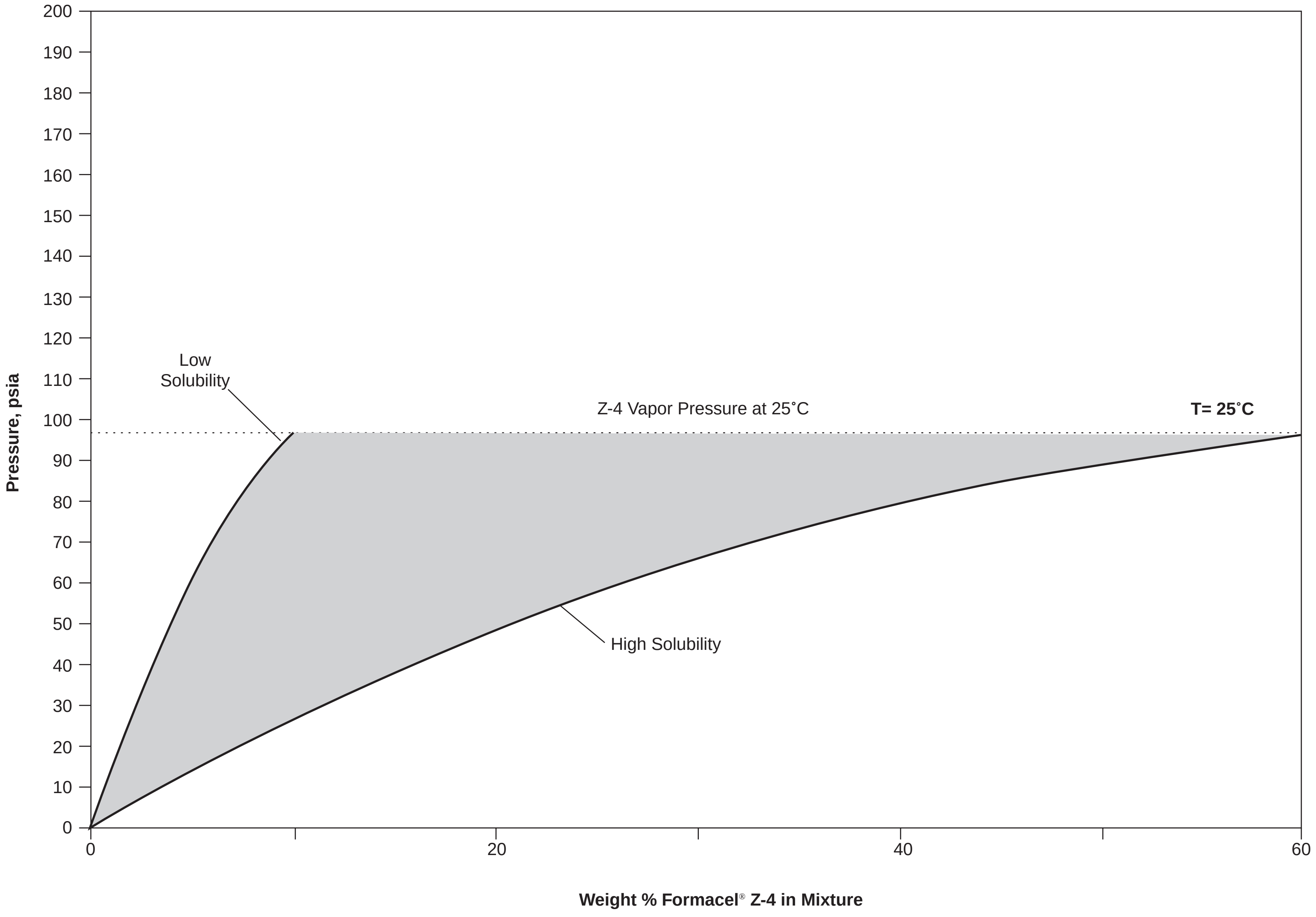


Figure 4B. Formacel® Z-4 in Polyether Polyols

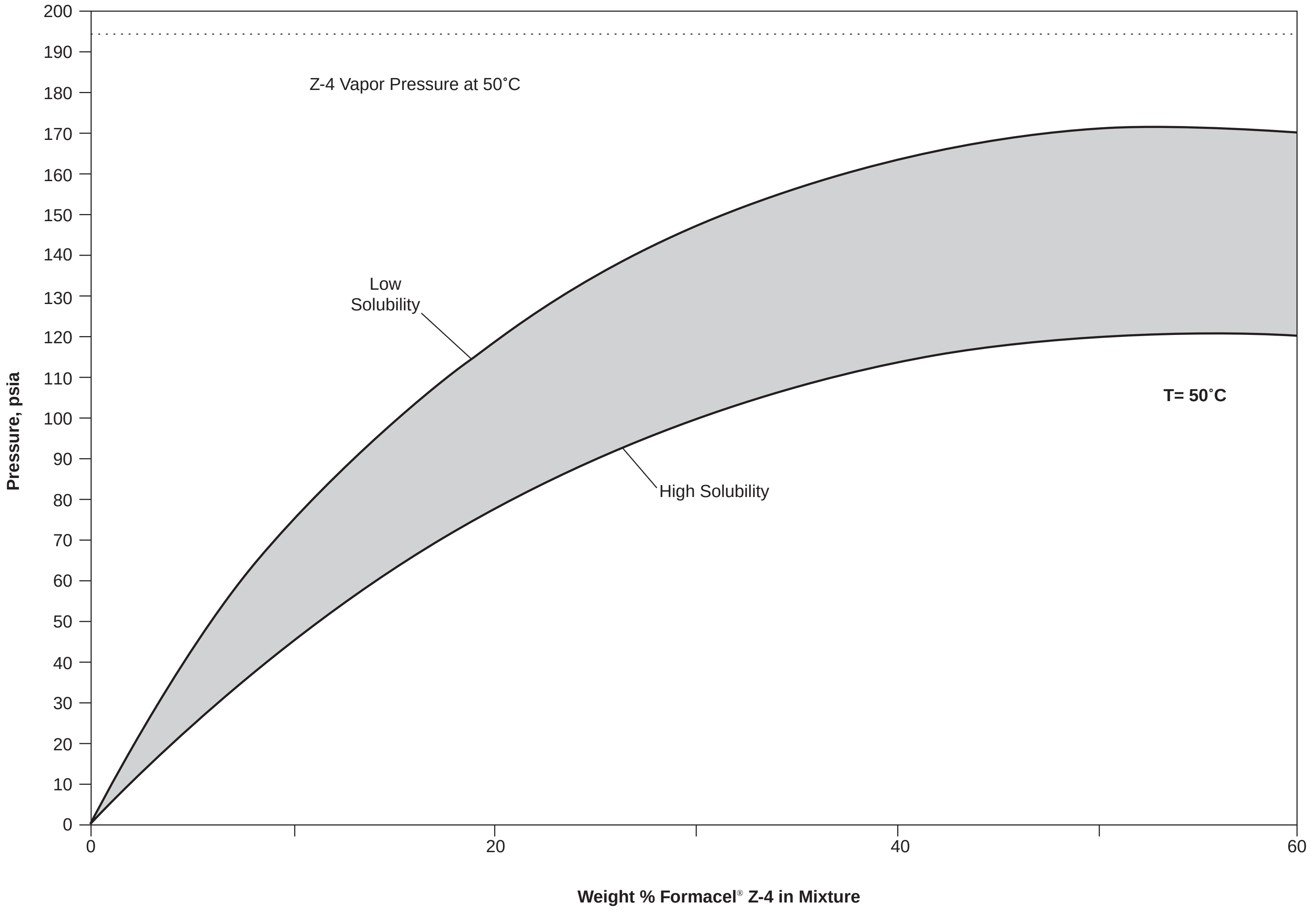


Figure 4C. Formacel® Z-4 in Polyether Polyols

Figure 5. Viscosity at Three Temperatures

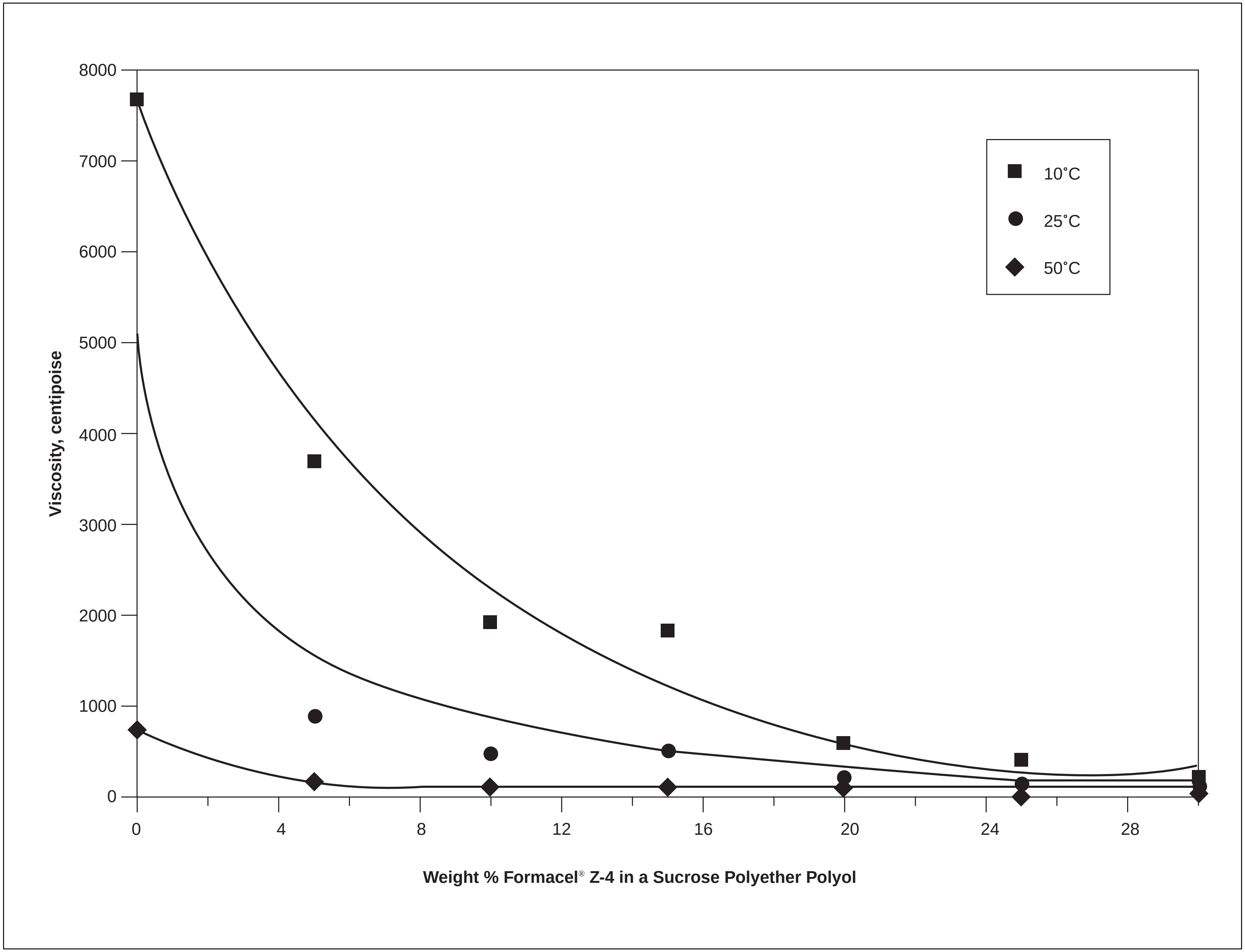


Table 4
Materials for Formacel® Z-2 and Z-4 Compatibility Testing

Elastomers List

Symbol	Material	Brand/Grade
EPDM	Hydrocarbon	Nordel®
T	Polysulfide	Thiokol® FA
FPM	Fluoroelastomer	Viton® A
U	Polyurethane	Adiprene® L
SPR	Styrene-Butadiene	Buna S
SI	Silicone	Silicone Rubber
CSM	Chlorosulfonated Polyethylene	Hypalon® 40
NR/IR	Polyisoprene	Natural Rubber
CR	Polychloroprene	Neoprene W
IIR	Isobutylene Isoprene	Butyl Rubber
NRB	Acrylonitrile Butadiene	Buna N

Plastics List

Symbol	Material	Brand/Grade
PE	Polyethylene	Alathon® 7050
MMA	Acrylic	Lucite® L
PA	Polyamide (Nylon)	Zytel® 101
TFE	Fluorocarbon	Teflon® TFE
PC	Polycarbonate	Tuffak®
ABS	Acrylonitrile-Butadiene-Styrene	Kralastic®
PS	Polystyrene	Styron® 475
EPX	Epoxy	Epoxy Resin
C	Cellulosic	Ethocel®
POM	Acetal	Delrin® 500
PVC	Polyvinyl Chloride	PVC Unplasticized

Table 5
Formacel® Z-2 and Z-4 Compatibility Test Results

Tested Materials Which Showed Some Effect from Exposure

Liquid Exposure @ Room Temperature		Vapor Exposure Room Temp.		Vapor Exposure 130°F	
134a	152a	134a	152a	134a	152a
Viton® A	Viton® A	N	N	N	N
Adiprene® L	Adiprene® L	O	O	O	O
Buna S	Buna S	N	N	N	N
	Thiokol® FA	E	E	E	E
	Silicone				
Lucite® L	Lucite® L				
Ethocel®	Ethocel®				
Styron® 475	Styron® 475				
	Kralastic®				

Table 6
Formacel® Z-2 and Z-4 Stability Test Results

	% Degradation (6 weeks at 60°)	
Catalyst	Z-2	Z-4
Amine	<0.001	<0.001
Potassium	<0.001	<0.001
Tin	<0.001	<0.001
Neutralized Amine	<0.001	<0.001

Test Conditions:

- 25 wt % HFC-134a or HFC-152a
- 2 parts catalyst per 100 parts polyol by weight
- 1 part water per 100 parts polyol by weight
- Type 1010 steel coupon

Permeation

For success in rigid insulation foams, good long term insulation value is required. This is partly accomplished by retaining the blowing agent in the cells as an insulating gas. Film permeation studies are underway to determine how well Formacel® Z-2 and Z-4 are contained by the polymers that form the cells. Tests have been completed with two polymers described in **Table 7**. The results of these experiments, thus far, indicate:

1. Permeation rates for the alternative blowing agents are comparable to those of CFC-11 in the polymers tested.
2. Permeation rats for the blowing agents vary with the chemistry and structure of the polymer. Thus, the formulation conceivably could be used to help control gas permeation, and consequently, thermal aging.
3. The ranking of blowing agent permeation rates changes from polymer to polymer. Thus, an insulating gas may be well contained in one formulation, but not as well contained in another.
4. The temperature dependence of the permeation rates varies from combination to combination. In fact, in some cases, the rats increase rapidly with increasing temperature.
5. As expected, the permeation rate for nitrogen is much faster relative to the other gases tested.
6. Of those tested, the slowest permeating gas in each polymer was Formacel® Z-4.

The results of these first two permeation studies are plotted in **Figures 6** and **7**. Overall, it appears that these comparative permeation rate experiments can help in designing formulations that could reduce or control thermal aging.

Processing Experiments

Polyurethane foam processing technology is typically designed for a blowing agent which is a liquid at ambient conditions. This type of process dispenses a liquid mixture which subsequently foams as the heat of reaction vaporizes the liquid blowing agent. Low-boiling blowing agents are sometimes used in small amounts to pre-expand or “froth” the liquid mixture; typically the “frothing agent” is CFC-12. The concept proposed here is to extend use of low-boiling blowing agents so that they alone are used to expand a polyurethane foam. The goal in this work is to understand the potential for replacing high-boiling CFC-11 with a low-boiling alternative.

Initial trials with Formacel® Z-4 as the blowing agent identified areas where additional development is necessary to achieve acceptable foam processing and product quality.

To begin, pressure-handling capabilities of the equipment must be evaluated. With CFC-11, B-sides are typically mixed and handled at atmospheric pressure. With gases, mixing and handling equipment must be able to contain the pressures developed. Usually this means providing a mixing tank and a process feed tank that are pressure-rated. The chemical processing equipment itself, in most cases, has the capability to contain low-boiling blowing agent B-side mixtures. Care must be taken, however, to individually evaluate each plant because these generalities do not always apply.

Table 7
Polymer Systems in Permeation Study

Designation	Application	Isocyanate	Polyol	Isocyanate Index
A	Insulation Board	MDI	Polyester (scrap PET-based)	250
B	Insulation Board	MDI	Polyester (phthalic anhydride-based)	250

Figure 6. Permeation Coefficients of HFCs

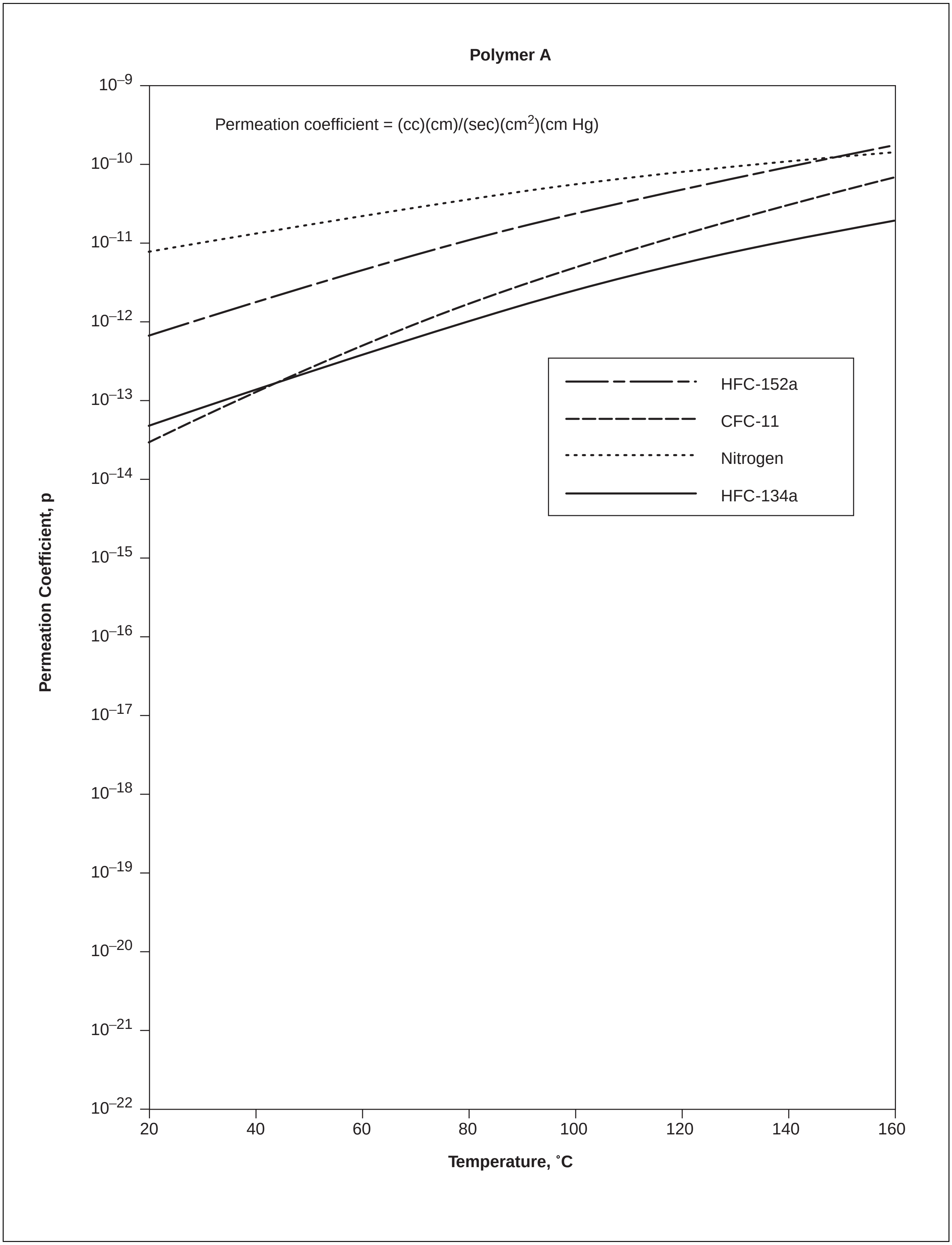
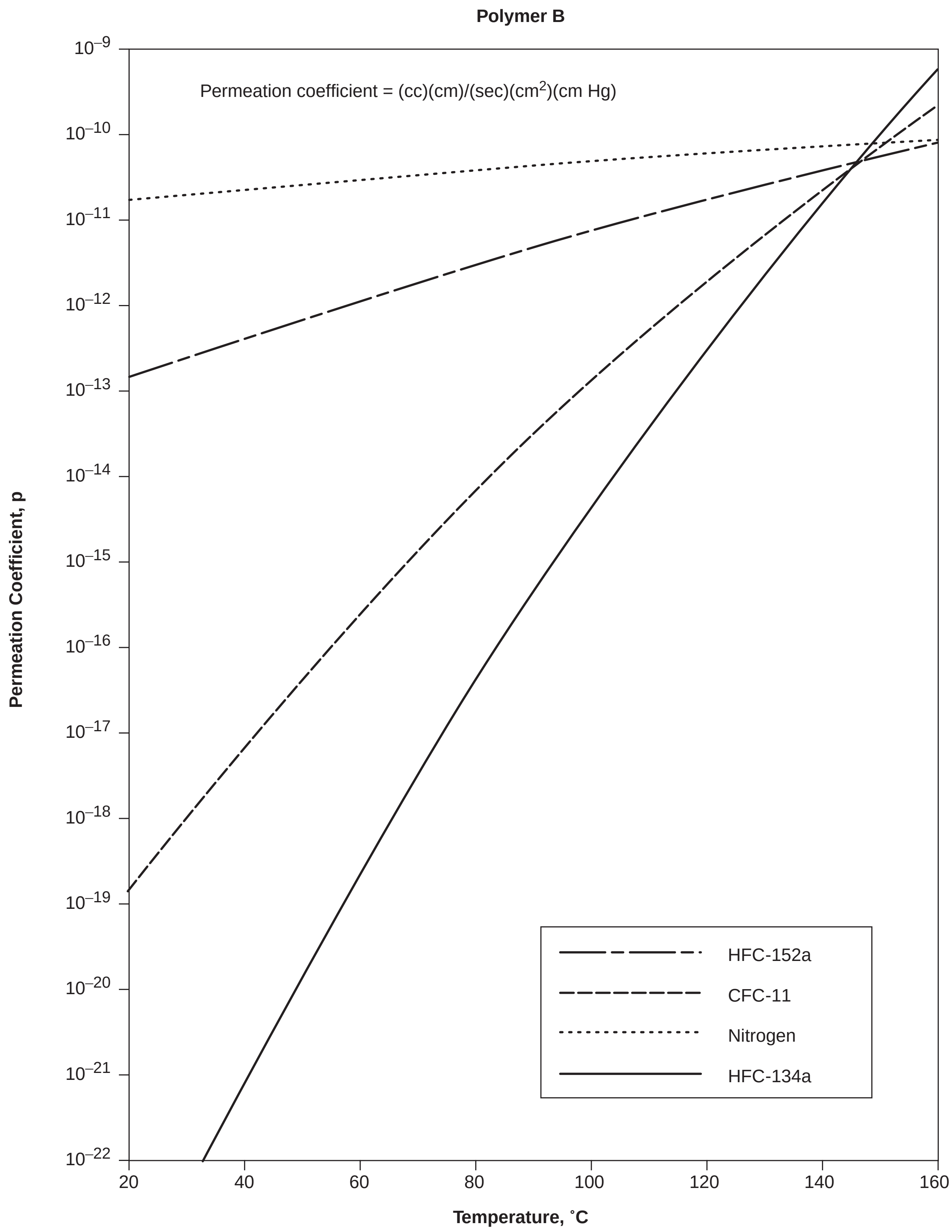


Figure 7. Permeation Coefficients of HFCs



The next area of consideration is mixing and pouring the foam. Using Formacel® Z-4 alone required high levels, 15–20%, in the foam to come close to typical 2 lbs/ft^3 (PCF) densities. Such a foam mixture dispenses from the mixhead as a froth foam. Since most equipment is designed to process a liquid mixture that flows before it expands, foaming with gases will require some changes in the way a mixture is poured and distributed. As pressure is let down in the mixhead, the blowing agent expands rapidly, so that voids tend to form in the foam from pockets of gas. The frothed mixture dispensed has body so that it will not distribute before fully expanding like a liquid mixture does. Both these differences affect the properties, particularly the insulation value, of rigid PUR and PIR foams. In contrast, low levels of gases have been manageable, and with assistance from a second blowing agent, good quality commercial polyurethane foams have been achieved.

Thus, early testing highlights two areas for continuing work to improve gaseous blowing agents' processibility in polyurethane foams:

- The foam formulation, which needs to be more tailored to the zero-ODP blowing agents.
- The mixhead, which must have the ability to dispense and distribute the foaming mixture while managing the blowing agent pressure letdown.

Overall conclusions for Formacel® Z-4 processing experiments, thus far, can be summarized as follows:

Promising quality foam was produced using Formacel® Z-4 in an appliance formulation with and without water. The polyether polyols used in the formulation were polyols that have had the best Z-4 compatibility of the ones tested so far.

Foams of the desired 1.9–2.0 lbs/ft^3 (PCF) density were produced using 2%–3% water and 5% Formacel® Z-4 by weight in the B-side mix.

The foams did contain voids and an occasional tear (from pockets of undissolved gas).

Initial k-factors of the foams were about 0.165 BTU·in/ft^2·HR·°F versus 0.12–0.13 desired.

Choice of isocyanate had an effect on void formation. There were less voids in the foam when the higher viscosity isocyanate was used. Higher reaction mixture viscosities during the early reaction stage could be improving the mixture's capability for containing the expanding gases.

Lower chemical feed temperatures improved foam quality as long as cooling the B-side did not cause the Formacel® Z-4 to come out of solution. At 80°F, the pour was more controlled and there were less voids in the foam than at 100–110°F pours.

With the HFCs, B-side addition and mixing are more difficult. There are Formacel® Z-4 solubility limits, beyond which a free phase of Z-4 forms. Typically, required Z-4 additions are beyond these limits. It may be necessary to form stable Z-4/polyol emulsions to provide a homogeneous B -side feed. These emulsions may, in fact, be a benefit in helping to "seed" formation of a more uniform foam cell structure. Different chemical and mechanical techniques are being evaluated to improve HFC/polyol mixing.

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