

Contrails

THEORETICAL AND EXPERIMENTAL EVALUATION OF POLYMERIC MATERIALS FOR USE IN A SPACE ENVIRONMENT

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Introduction

Expandable solar concentrators and other expandable space-vehicle structures will require utilization of polymeric materials in the form of films, foams, and coated fabrics. These materials must withstand ultraviolet radiation, vacuum, temperature extremes, and numerous other elements of the space environment without undergoing volatilization or degradation to a critical degree.

While much is known about the properties of materials in the earth's normal atmosphere, only a meager amount of information is available on how common polymeric structural material properties will be affected by the hyper-environmental conditions of outer space.

Ultraviolet Radiation Considerations

The absorption of ultraviolet radiation causes displacement of outer electrons in the molecule. However, if there is no simple electronic, atomic, or molecular change that can use the exact amount of energy contained in a photon of ultraviolet radiation, there may be no interaction and no chemical or physical change. Unfortunately in all the polymeric molecules, ultraviolet radiation is absorbed to some degree and its action manifests itself as dissociation of the particular plastic or rubber chain.

In general, the ultraviolet decomposition of polymers so far investigated appears to be due to typical chain reactions that involve free-radical intermediates. When these free-radical intermediates can react with a material such as oxygen, a termination reaction is effected which stabilizes these lower-molecular-weight intermediates. With this lowering in molecular weight is associated a decrease in the load-carrying ability of the polymer.

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Early ultraviolet exposure studies on typical elastomeric compounds were made with a fadeometer. Following exposure stress-strain characteristics were measured and compared with original values. Results obtained on some of the elastomers are summarized in Table I.

These results indicated that butyl and neoprene were candidates for more extensive degradation studies. These rubbers with slightly different compounding were then irradiated with ultraviolet under high-vacuum conditions. Several unseamed and seamed film specimens were also investigated in the same manner.

The irradiation equipment used for these studies consisted of a diffusion pumping system with a mechanical pump and a liquid nitrogen cold trap. The vacuum chamber is an 18-inch-diameter, 30-inch-high Pyrex bell jar mounted on a 20-inch-diameter stainless steel plate. This system has a capability of attaining pressures of approximately 5×10^{-7} mm Hg, with the use of the liquid-nitrogen trap (see Figure 1).

The ultraviolet source used in the evaluation was a 250-watt quartz tube, mercury-vapor lamp, General Electric type UA-2. According to the manufacturer the lamp produces ultraviolet radiation with wavelengths from 2200 to 4000 Angstroms. Visible and near infrared radiation is also produced by the lamp. However, complete data on the infrared region are not available.

The UV lamp was mounted in a vertical position in the center of a specially designed 14-inch inside-diameter cylindrical water-cooled specimen holder (see Figure 1). It was found that with the use of the water-cooled holder the temperature of the test specimens could be maintained between 85°F and 95°F. Without cooling, equilibrium temperatures were on the order of 300°F.

The results of these exposures are presented in Tables II, III, and IV. Data obtained for the elastomers are also displayed graphically in Figures 2 and 3.

These previous data were obtained at pressures in the 10^{-5} mm Hg and 10^{-6} mm Hg regions, as shown in Figure 4. The fact that much lower pressures exist in space leads one to predict that even more extensive degradations would occur. This is not necessarily the case. Under our test conditions we have by comparison a huge concentration of chain terminators such as oxygen which will stabilize the dissociated polymer. However, if there is nothing for these free-radical fragments to react with they will react with themselves. In this way a cross linking and actual stabilization or improvement of polymer properties could be achieved.

We have obtained preliminary molecular weight data (Table V) in this area and intend to expand our research along these lines.

TABLE I

1000-HOUR ULTRAVIOLET EXPOSURE OF RUBBERS
AT ATMOSPHERIC PRESSURE

Elastomer	Original		Exposed	
	Tensile (psi)	Elongation (%)	Tensile (psi)	Elongation (%)
Butadiene-Acrylo- Nitrile	1940	240	1830(94)	170(74)
Butyl	2140	525	2419(113)	560(107)
Neoprene W	1910	600	1642(85)	550(97)
SBR	2635	610	2095(80)	360(36)

Figures in parenthesis represent per cent of original value retained after exposure.

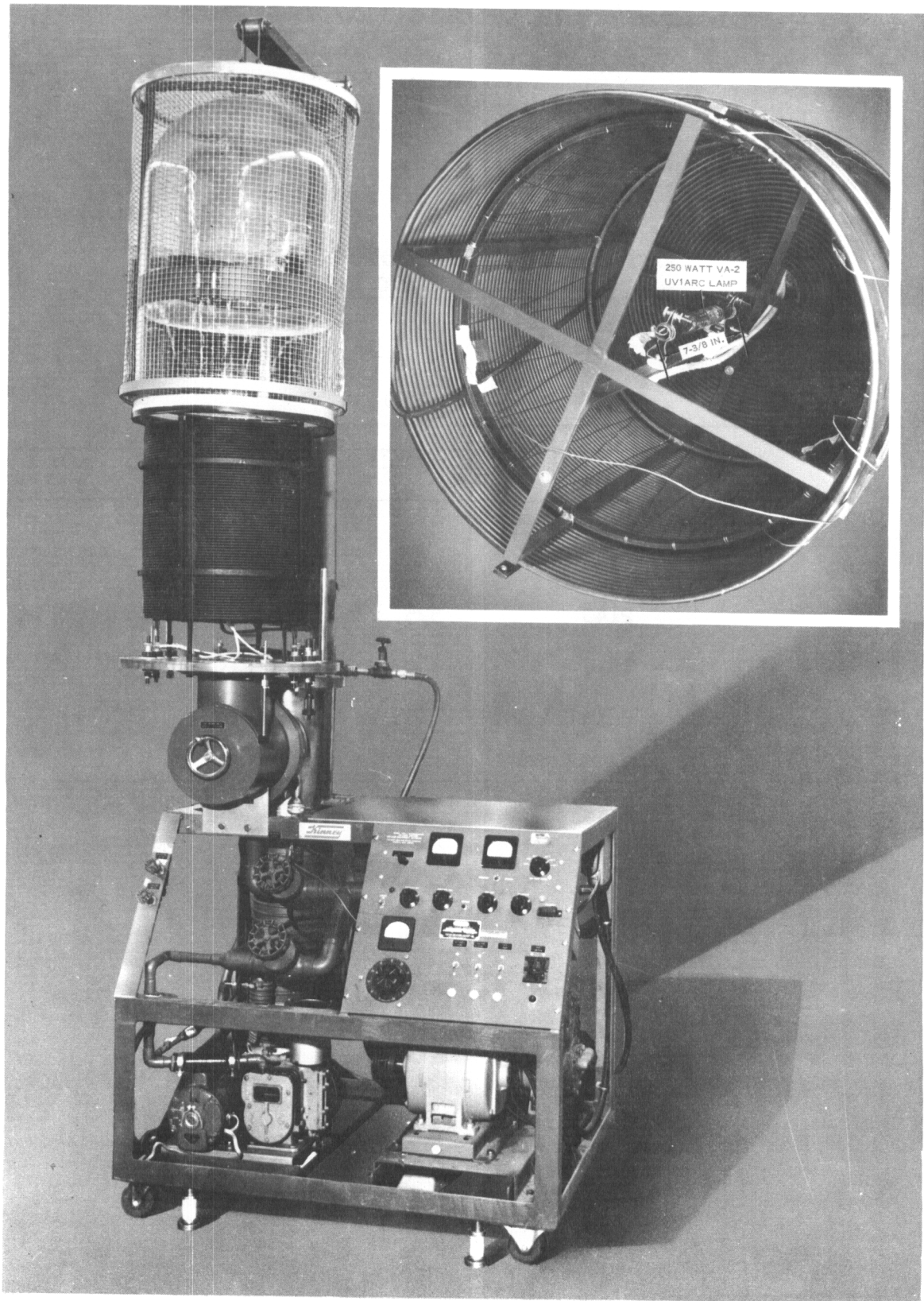


Fig. 1 High vacuum bell jar with ultra-violet source

TABLE II
EFFECTS OF VACUUM AND OF VACUUM WITH
ULTRAVIOLET RADIATION ON ELASTOMERS*

Material	Type of Exposure**	Temperature (°F)	Exposure Time (hr.)	Weight Change (per cent)	Tensile Strength		Breaking Elongation			
					Before Exposure (psi)	After Exposure (psi)	Before Exposure (in./in.)	After Exposure (in./in.)		
Butyl	Vacuum	80	24	+ 0.10	2315	2616	+ 13.0	0.880	0.820	-6.8
	Vacuum	80	96	+ 0.22	2315	2420	+ 4.5	0.880	0.845	-4.0
	Vacuum	80	312	+ 0.09	2315	2441	+ 5.4	0.880	0.805	-8.5
	Vacuum and ultraviolet	155	24	- 1.59	2315	2572	+ 11.1	0.880	0.790	-10.2
	Vacuum and ultraviolet	155	96	- 4.04	2315	2626	+ 13.4	0.880	0.755	-14.2
	Vacuum and ultraviolet	155	312	- 4.04	2315	2710	+ 17.1	0.880	0.650	-26.1
Neoprene	Vacuum	80	24	+ 0.04	2288	2378	+ 3.9	0.515	0.525	+ 1.9
	Vacuum	80	96	- 0.14	2288	2306	+ 0.8	0.515	0.532	+ 3.3
	Vacuum	80	312	- 0.93	2288	2286	- 0.1	0.515	0.518	+ 0.6
	Vacuum and ultraviolet	155	24	- 3.27	2288	2558	+ 16.2	0.515	0.428	-16.9
	Vacuum and ultraviolet	155	96	- 5.93	2288	2568	+ 12.2	0.515	0.302	-41.3
	Vacuum and ultraviolet	155	312	- 5.95	2288	2858	+ 25.0	0.515	0.335	-35.0

* Values are averages of two specimens.
** Maximum vacuum pressures on the order of 1×10^{-5} mm. Hg.

TABLE III
EFFECTS OF VACUUM AND OF VACUUM WITH ULTRAVIOLET RADIATION ON FILMS

Material	Type of Exposure*	Temperature (F)	Exposure Time (hr)	Weight Change (per cent)	Tensile Strength		Change (per cent)	Break Elongation	
					Before Exposure (psi)	After Exposure (psi)		Before Exposure (in./in.)	After Exposure (in./in.)
Polyethylene terephthalate, aluminumized one side	Vacuum	75 to 80	168	- 0.02	25,200	23,600	- 6.4	1.08	0.96
	Vacuum	55 to 60	770	+ 0.04	26,200	23,000	- 12.2	1.414	1.039
	Vacuum and ultraviolet	85 to 95	770	+ 0.37	26,200	14,900	- 43.0	1.414	0.174
Polyvinyl fluoride, type 20, clear	Vacuum	75 to 80	168	Not measurable	12,150	12,375	+ 1.9	1.112	1.135
	Vacuum	55 to 60	770	+ 0.29	14,700	13,400	- 8.8	0.965	0.915
	Vacuum and ultraviolet	85 to 95	770	- 1.57	14,700	10,500	- 28.7	0.965	0.296

*Maximum vacuum pressures on the order of 5×10^{-6} mm Hg.

TABLE IV
EFFECTS OF VACUUM AND OF VACUUM WITH ULTRAVIOLET RADIATION ON
SEALED FILMS* (EXPOSURE TIME OF 770 HR)

Material	Type of Exposure**	Temperature (F)	Weight Change (per cent)	Tensile Strength		Change (per cent)
				Before Exposure (psi)	After Exposure (psi)	
Polyethylene terephthalate, 1 mil, aluminized one side, butt sealed with 1/2-in. heat-sealable, polyester-resin-coated polyethylene-terephthalate tape	Vacuum	55 to 60	0.00	22,200	22,100	- 0.2
	Vacuum and ultraviolet	85 to 95	+ 0.24	22,200	15,600***	- 29.5
Polyethylene terephthalate, 1 mil, aluminized one side, butt sealed with 3/4-in. pressure-sensitive, silicone-adhesive-coated polyethylene-terephthalate tape	Vacuum	55 to 60	+ 0.06	15,000	15,100	+ 0.7
	Vacuum and ultraviolet	85 to 95	+ 0.08	15,000	15,800***	+ 5.3
Polyethylene terephthalate, 1 mil, aluminized one side, butt sealed with 1/2-in. polyethylene-terephthalate tape and solvent-type adhesive	Vacuum	55 to 60	- 0.57	15,600	16,900	+ 8.1
	Vacuum and ultraviolet	85 to 95	- 1.13	15,600	8,100	- 48.3
Polyethylene terephthalate, 1 mil, aluminized one side, butt sealed with 1/2-in. polyethylene-terephthalate tape and Pliobond [†] solvent-type adhesive	Vacuum	55 to 60	- 0.71	19,500	21,300	+ 9.4
	Vacuum and ultraviolet	85 to 95	- 3.23	19,500	14,700***	- 24.5
Polyvinyl fluoride, 1 mil, clear, 1/16-in. lap-seamed, heat-sealed	Vacuum	55 to 60	+ 0.04	9,400	9,600	+ 2.1
	Vacuum and ultraviolet	85 to 95	- 1.48	9,400	9,800	+ 5.0

* All values are the averages of three specimens. †Tapes applied to nonaluminized side.

**Maximum vacuum pressures on the order of 5 x 10⁻⁶ mm Hg.

***Specimen failure did not occur in seam.

† Goodyear Pure and Rubber Company adhesive.

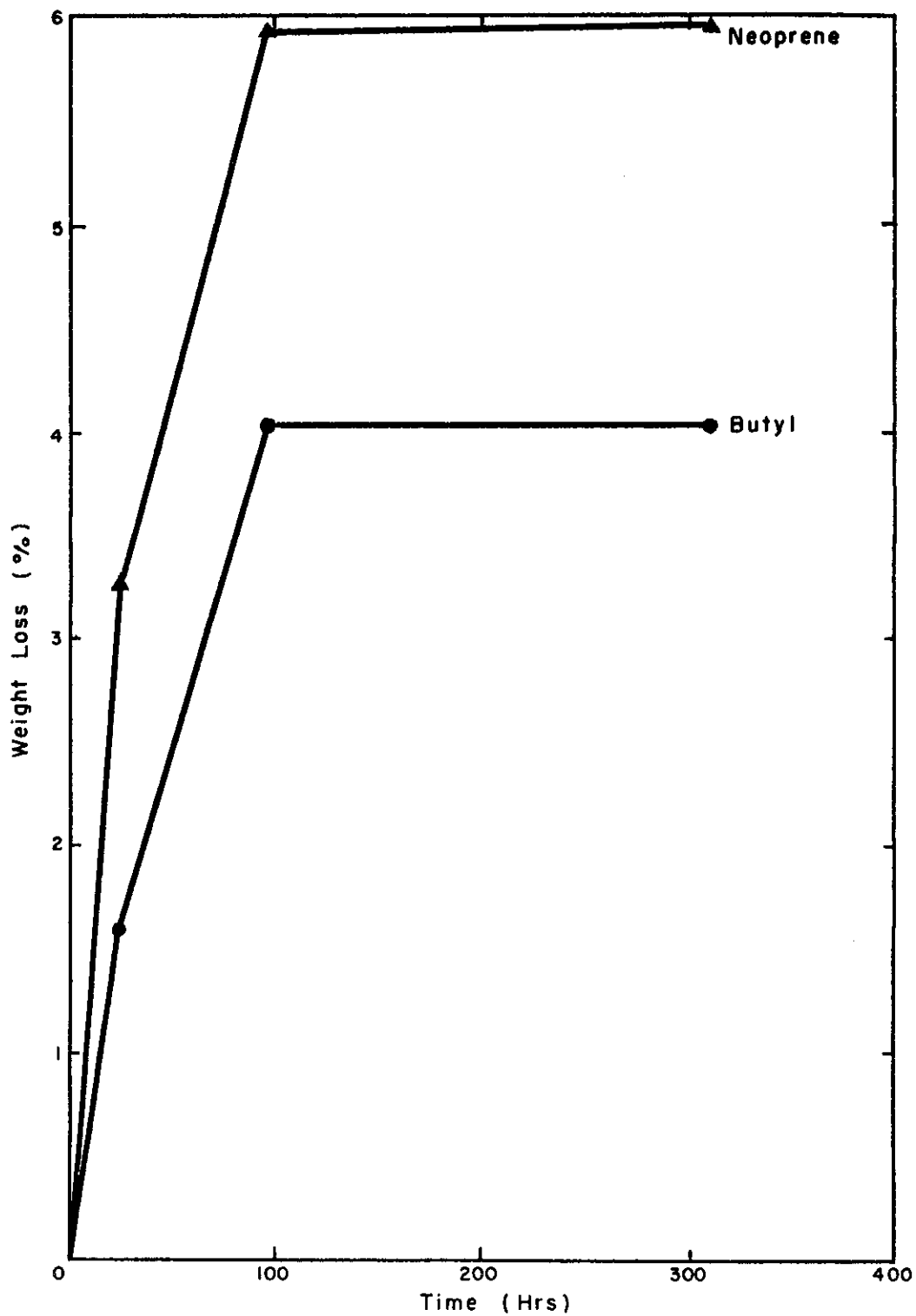


Figure 2 - Change in Weight of Elastomers After Exposure to High Vacuum and Ultraviolet

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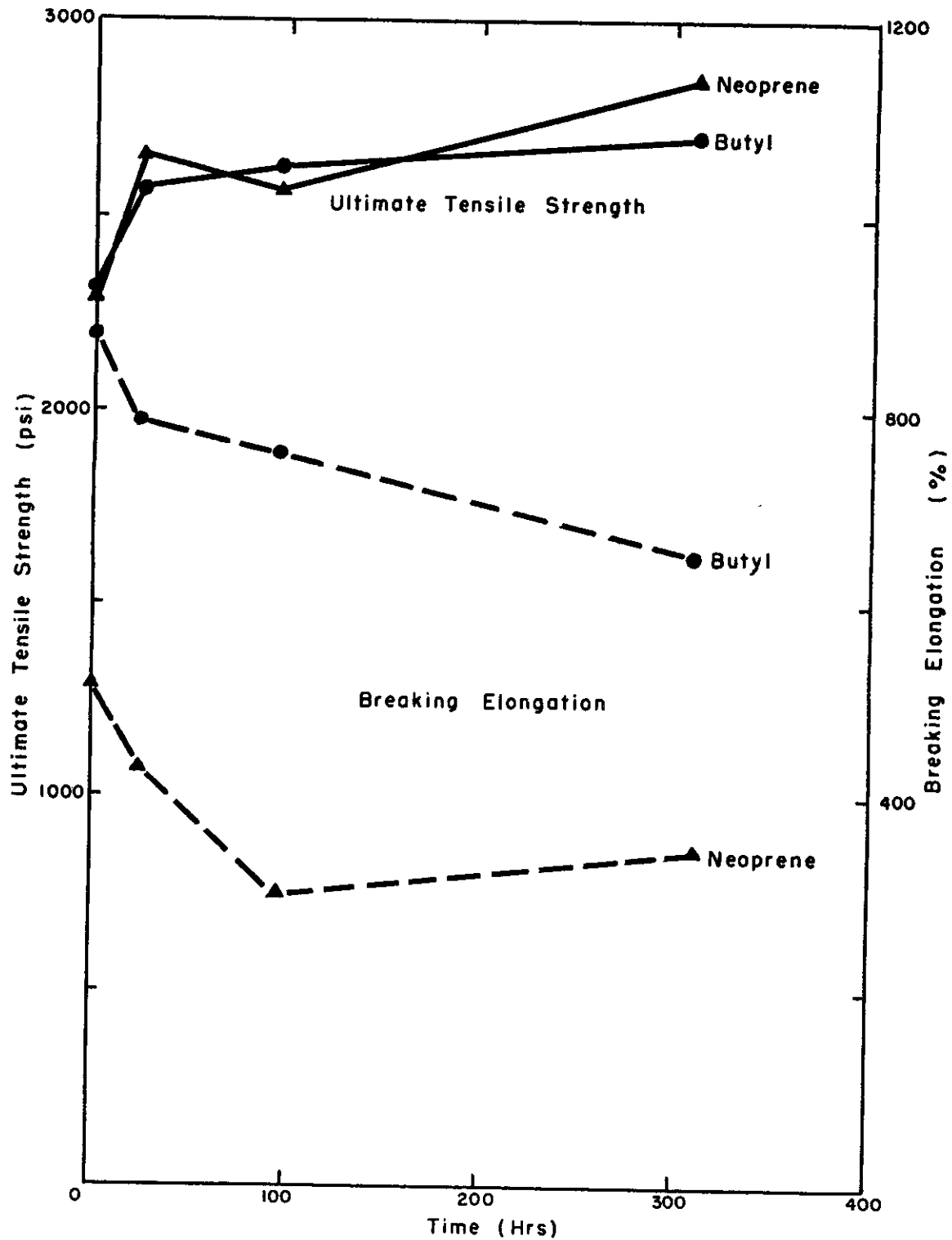


Figure 3 - Change in Strength and Elongation of Elastomers After Exposure to High Vacuum and Ultraviolet

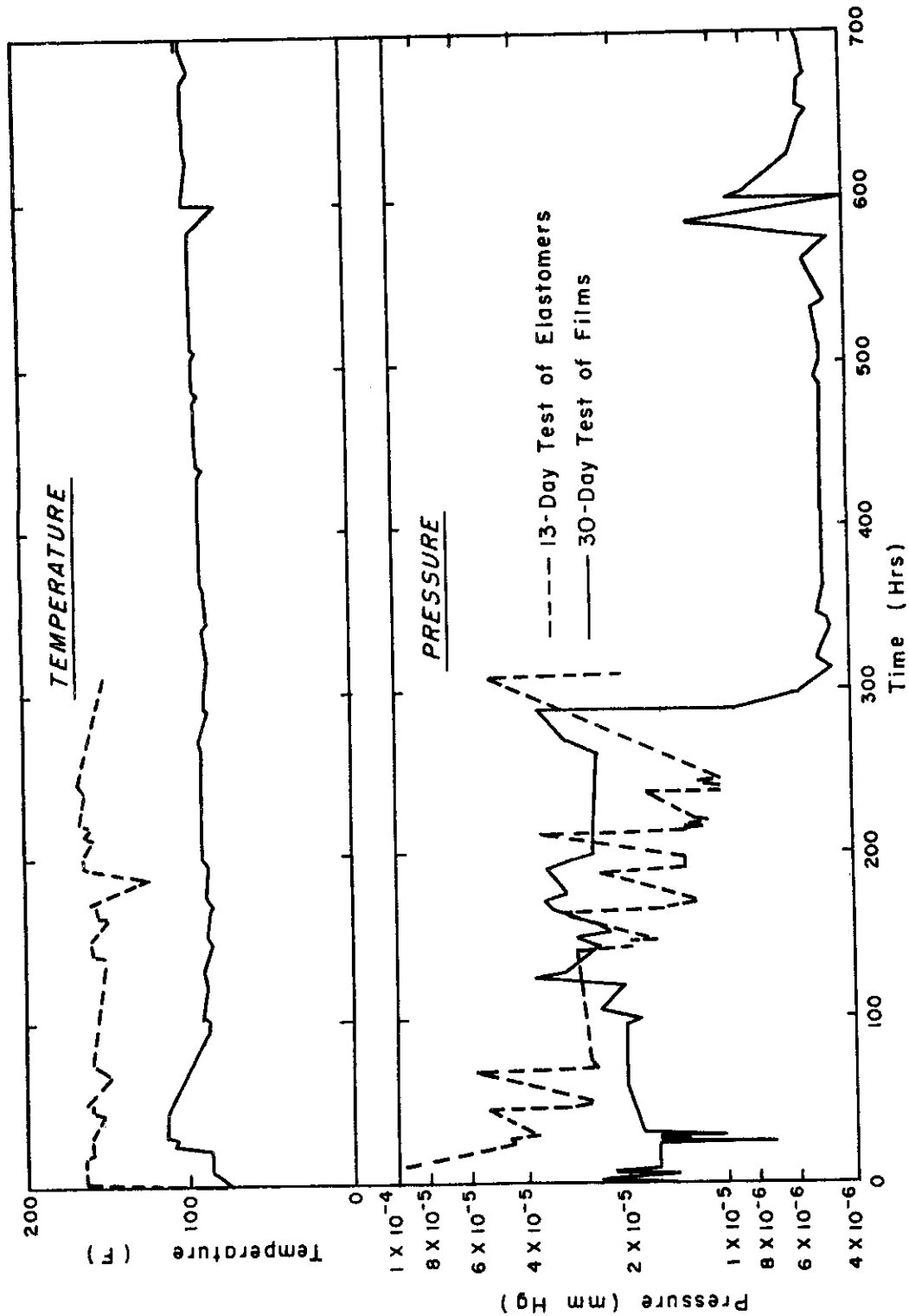


Figure 4 - Typical Curves of Specimen Temperature and Vacuum-Chamber Pressure for Ultraviolet and Vacuum Exposure Tests

TABLE V
EFFECT OF ATMOSPHERE AND UV RADIATION ON POLYMER
MELT VISCOSITY MOLECULAR WEIGHT

Polymer	M.W. After 72 Hrs UV Exposure in Air (% of Original)	M.W. After 72 Hrs UV Exposure in H ₂ (% of Original)
Polyethylene terephthalate	60	68
Polypropylene	21	86

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A comment is in order relative to the merits of weight loss measurements as criteria of polymer performance under hyper-environmental conditions. Frequently a simple distillation of a low molecular-weight fraction leaves behind an enhanced polymer. In cases where weight loss is a function of dissociation of chains, this usually means that a small end fragment is distilling out but that the remainder of the chain is intact. If such a degradation process is arrested it would not prove harmful. On the other hand if the chain scission occurred in the middle of a chain rather than at the ends, we would have no weight loss but there would be a substantial decrease in polymer physical properties. Therefore it is conceivable that in many cases weight-loss degradation is the preferred type.

Polymer Volatility

There has been concern expressed that polymers might distill away in space and for that reason only metals or ceramics could have utility. This fear stemmed from the fact that pressures drop significantly with increasing altitudes as shown in Figure 5.

This concern led us to apply theoretical considerations to just what is the vapor pressure or boiling point of a given polymer. By referring to P.A. Small's* work on solubility parameters of polymers from cohesive energy densities, it is possible to calculate an order of magnitude for heats of vaporization of various polymers. The following relationship developed by Small was employed:

$$\Delta H_v = RT + V \delta^2$$

where ΔH_v = Molar heat of vaporization

R = Gas constant

T = Absolute temperature

V = Molar volume

δ = Solubility parameter of polymer

When applying this equation to polymers the fact that they have a molecular weight distribution makes it difficult to calculate molar volume. However, let us assume that polyethylene terephthalate contained a fraction which was only 1000 molecular weight. Using Small's equation,

$$\Delta H_v \approx 2T + \frac{1000}{1.38} (10.7)^2, \text{ and Trouton's rule, } \frac{\Delta H_v}{\text{Absolute boiling pt}} = 27,$$

we find that the boiling point is 3319°K.

*P. A. Small, Journal of Applied Chemistry, 3 71-80 (1953)

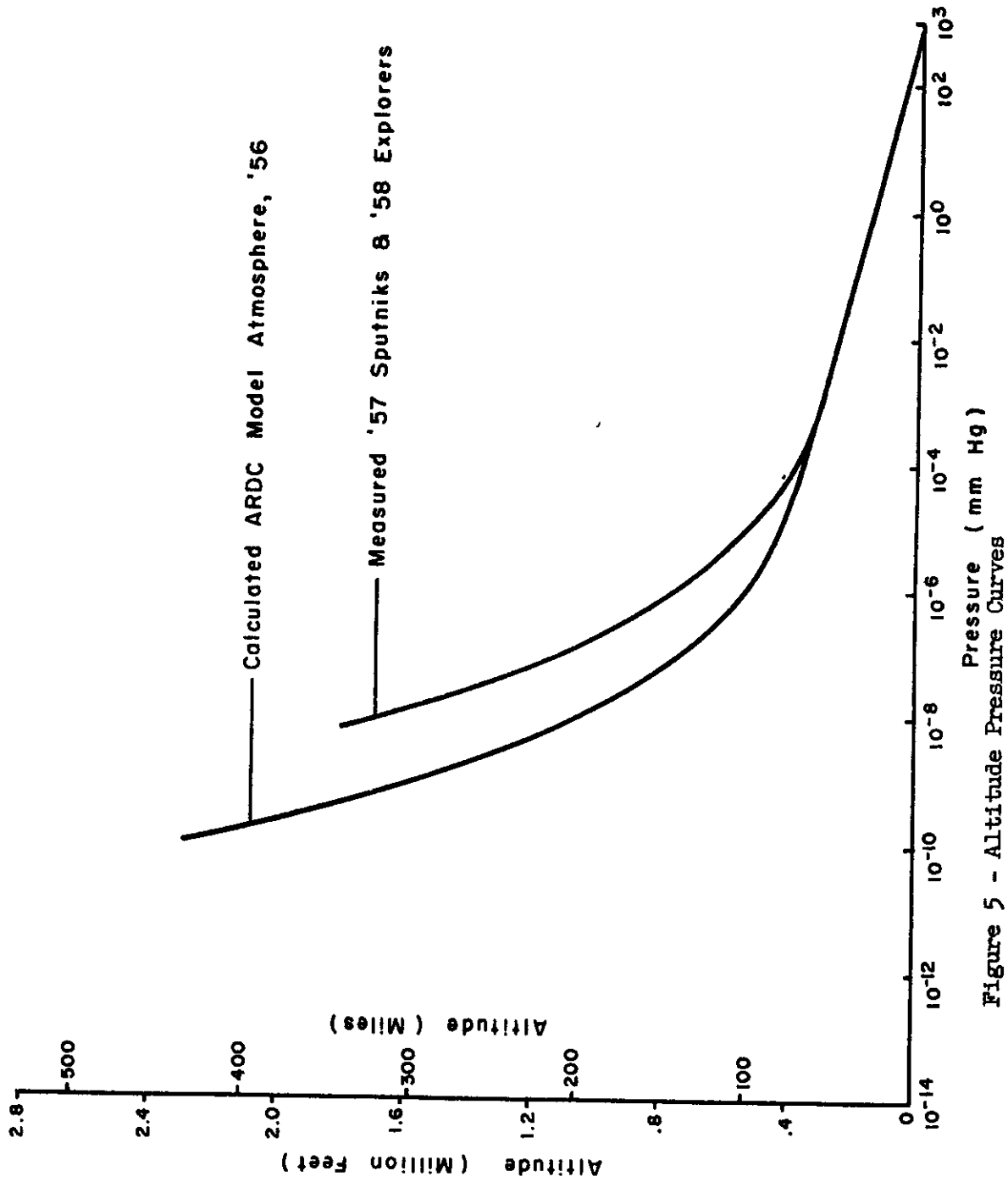


Figure 5 - Altitude Pressure Curves

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A calculation of the vapor pressure of this 1000 M.W. polyethylene terephthalate at any temperature can be made using the Clausius-Clapeyron equation, $\log p = \frac{-\Delta H_v}{2.303 RT} + C$.

C is an integration constant which can be evaluated by making use of the values just calculated above.

$$\begin{aligned}\Delta H_v &= (2)(3319) + \frac{(1000)}{(1.38)} (10.7)^2 \\ &= 89,600 \text{ cal/mol.}\end{aligned}$$

$$\begin{aligned}\text{Then } \log p &= \frac{-89,600}{(2.303)(2)(3319)} + C \\ \log 760 &= -5.86 + C \\ C &= 8.74\end{aligned}$$

To calculate the vapor pressure at a temperature of 125°C for this 1000 M.W. polyethylene terephthalate we find that

$$\begin{aligned}\log p &= \frac{-89,600}{(2.303)(2)(398)} + 8.74 \\ &= -4.0\end{aligned}$$

This means the vapor pressure of this 1000 M.W. polymer is of the order of $10^{-4.0}$ mm Hg.

This type of calculation provides us with an order of magnitude for vapor pressures. The fact that they are so low for even a 1000 molecular-weight polymer shows how ridiculous it is to be concerned about polymer volatility. It is obvious that, so long as there is no decomposition, polymers have lower volatility than metals.

Mechanical Behavior Aspects

In the selection of polymeric substances for use in space it is becoming increasingly important to consider also their mechanical behavior. For example, the ultraviolet resistance of a given polymer is much greater when the polymer is oriented.

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Another important consideration is the glass temperature, or T_g , of a polymer. Amorphous polymers above this temperature are rubbers, but below it they are hard and brittle, or plastics. This transformation from a rubber to a plastic is equivalent to the solidification of a liquid to a glass and hence the name glass-transformation temperature. It is not a phase change. Crystalline polymers such as polyethylene terephthalate also have a T_g , but the transition from a crystalline rubber to a crystalline plastic is not as visibly obvious as the change from an amorphous rubber to an amorphous plastic. The strengths of amorphous polymers are higher in the glass state, but even so they are significantly less than those of oriented crystalline rubbers or plastics.

In our selection of polymers for use in unmanned expandable space vehicles, rigidity of the polymer is often of prime importance. Because of this need, we have evaluated rigidity or stiffness as a function of density and glass temperature for a number of high polymers. We would like to discuss the results obtained on two such polymers, polyethylene terephthalate and polypropylene. First of all we develop the relationship for stiffness of a polymer in the following way:

$$\text{Stiffness} = k_1 E t^3$$

Where E = flexural modulus

and t = thickness

Thickness (t) is found by using the following equation:

$$W = k_2 t \rho \quad (\text{area constant})$$

where W = weight of polymer involved

and ρ = density.

$$\text{Therefore, Stiffness} = \frac{k_3 E W^3}{\rho^3}$$

$$\text{or } \frac{\text{Stiffness}}{W^3} \propto \frac{E}{\rho^3}$$

For equal weights of material, therefore

$$\text{Stiffness} \propto \frac{E}{\rho^3}$$

In Table VI physical test data on biaxially oriented 1/2-mil films of polyethylene terephthalate and polypropylene are recorded. The stiffness or rigidity as shown is calculated from the modulus data according to the equation $\text{Stiffness} \propto E/\rho^3$.

TABLE VI

PHYSICAL PROPERTIES OF POLYETHYLENE TEREPHTHALATE
AND POLYPROPYLENE

	Polyethylene Terephthalate	Polypropylene
Tensile at 25°C (psi)	19,000 and 17,000	29,000 and 14,000
Tensile at 125°C (psi)	13,000 and 9,600	20,000 and 10,500
Modulus at 25°C (psi)	500,000	200,000
Modulus at 125°C (psi)	100,000	120,000
Stiffness, polypropylene/polyethylene terephthalate at 25°C =	1.42	
Stiffness, polypropylene/polyethylene terephthalate at 125°C =	4.64	

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It is noted from the preceding table that at 25°C polypropylene is only 1.42 times stiffer than polyethylene terephthalate, but at 125°C polypropylene is 4.64 times more rigid. This is readily explained by the fact that at 25°C we are evaluating polyethylene terephthalate below its T_g and hence it is behaving as a crystalline plastic; polypropylene is being evaluated above its T_g and hence as a crystalline rubber. At 125°C polyethylene terephthalate is a crystalline rubber also, and the high modulus and strength associated with its glass state are no longer contributing.

These types of considerations are important ones to those of us in the inflatable structures fields, particularly under conditions where maximum rigidity is required.

Conclusions

As we approach the concluding phases of this paper, it is apparent that what we have stressed are basic principle considerations that must be made in selection of polymers not only for self-supporting applications but also for coatings as well. When we speak of ultraviolet resistance of a given polymer, we must stipulate not only the atmosphere of exposure but also the molecular weight and physical state of the polymer involved.