N85-32411

POLYMER-WATER INTERACTION STUDIES

WILKES COLLEGE

John Orehotsky

Corrosion in Solar Cells

REQUIREMENTS FOR CORROSION

- DISSIMILAR MATERIALS
- CELL-TO-CELL POTENTIAL DIFFERENCES
- ELECTRICALLY CONNECTED CELLS
- IONIC CONDUCTING ELECTROLYTE (POLYMER)

Ions in Polymers

- ABSORBED WATER IONS
- POLYMER IONS
- PLASTICIZER IONS
- UV ABSORBER AND STABILIZER IONS
- CROSS – LINKING AGENT IONS
- CHAIN SCISSION (IONIZING RADIATION) IONS

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Studies

ORIGINAL PAGE IS
OF POOR QUALITY

I – WATER ABSORPTION AND DESORPTION KINETICS IN EVA AND PVB

II – HUMIDITY DEPENDENCE OF ELECTRICAL PROPERTIES OF EVA AND PVB

III – PLASTICIZER EFFECTS IN PVB

IV – RADIATION EFFECTS IN PVB AND EVA

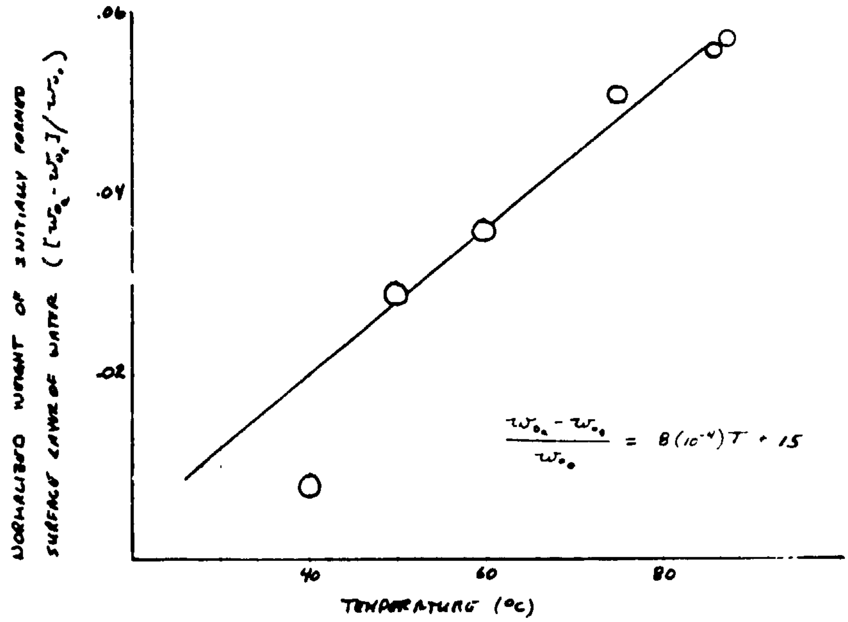
WATER ABSORPTION AND DESORPTION KINETICS IN PVB AND EVA

Weight Characteristics of EVA During Absorption and Desorption

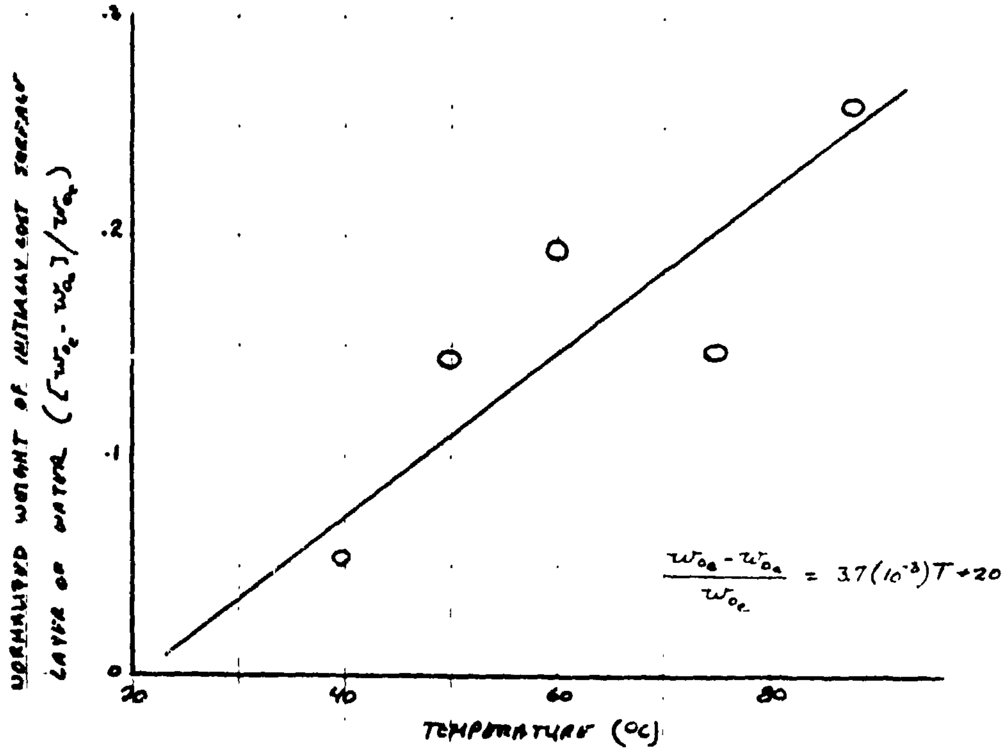
Temperature Humidity Conditions T(°C)/H (%)	Woe: Expected Starting Weight (gms)	Woa: Measured Starting Weight (gms)	W∞: Measured Final Weight (gms)	W∞-Woa: Apparent Weight Change (gms)	W∞-Woe: True Weight Change (gms)	Woa-Woe: Weight of Initially Formed Surface Layer (gms)	Woe-Woa: Weight of Initially Lost Surface Layer (gms)
88/0→88/100 absorption	1.600*	1.691	2.366	.675	.746	.091	—
88/100→88/0 desorption	2.366	1.750	1.599	.151	.767	—	.616
75/0→75/100 absorption	1.821*	1.914	2.804	.890	.983	.093	—
75/100→75/0 desorption	2.604	2.388	1.824	.564	.980	—	.416
60/0→60/100 absorption	1.520*	1.575	2.593	1.018	1.073	[illegible]	—
60/100→60/0 desorption	2.593	2.092	1.519	.573	1.074	—	.501
50/0→50/100 absorption	1.600*	1.647	2.565	.918	.965	.047	—
50/100→50/0 desorption	2.565	2.198	1.602	.596	.963	—	.367
40/0→40/100 absorption	1.608*	1.613	2.295	.682	.695	.013	—
40/100→40/0 desorption	2.295	2.149	1.603	.546	.692	—	.146

* Original weight of desiccated dried sample.

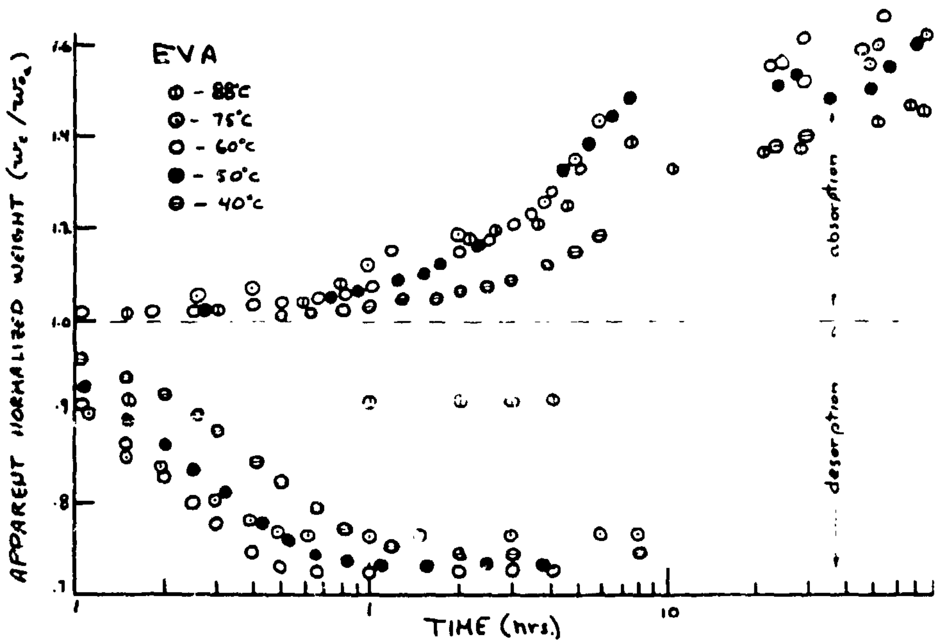
TEMPERATURE DEPENDENCE OF THE NORMALIZED WEIGHT FOR THE INITIALLY FORMED SURFACED LAYER OF WATER DURING WATER ABSORPTION IN EVA



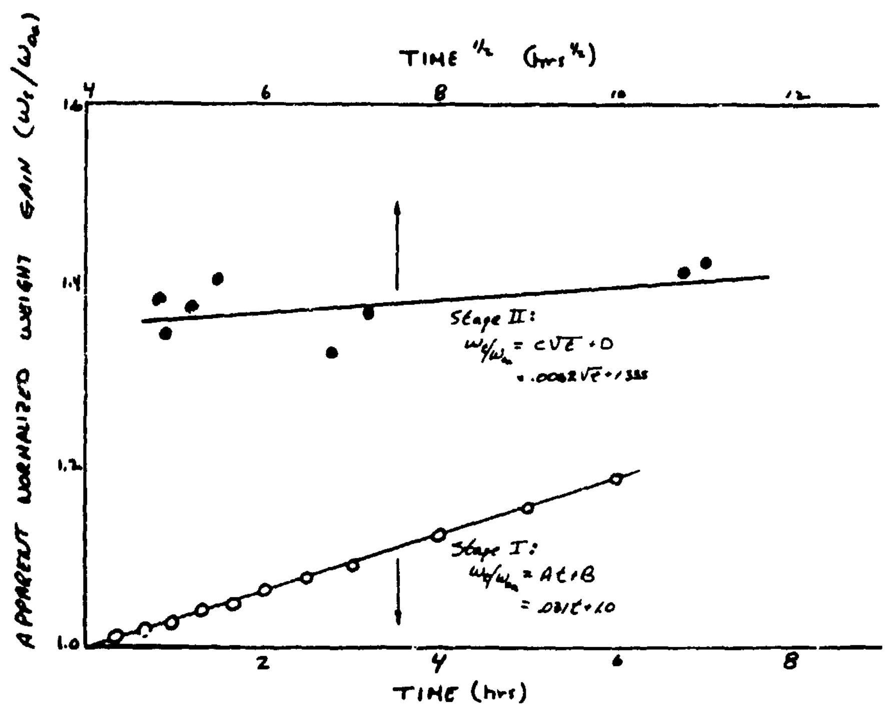
Temperature Dependence of the Normalized Weight for the Initially Lost Surface Layer of Water During Desorption in EVA



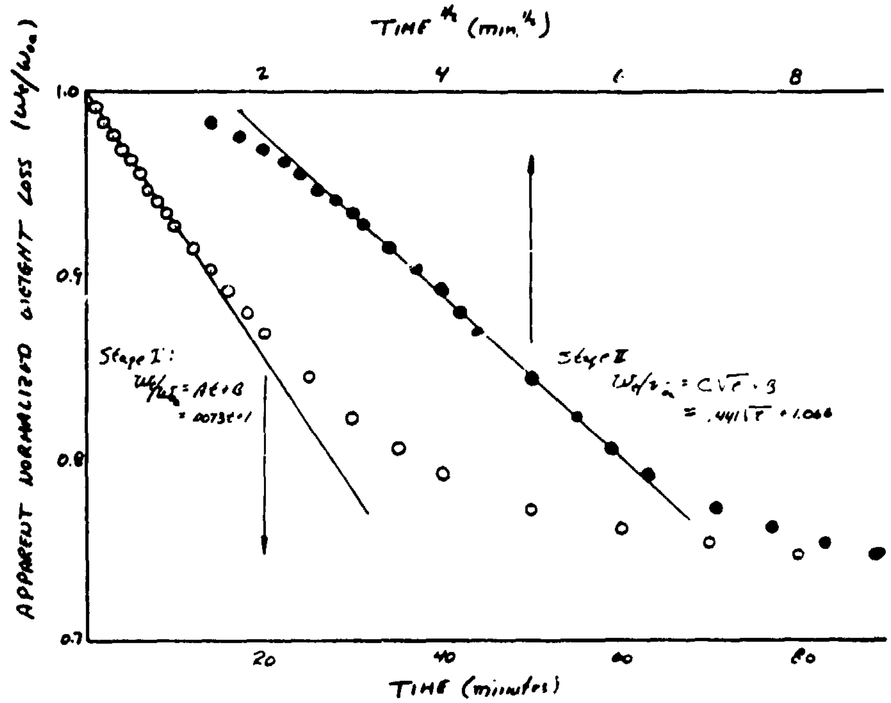
Normalized Weight Change During Absorption and Desorption in EVA



Time Dependence of Normalized Weight Gain in EVA Due to Water Absorption (40°C)



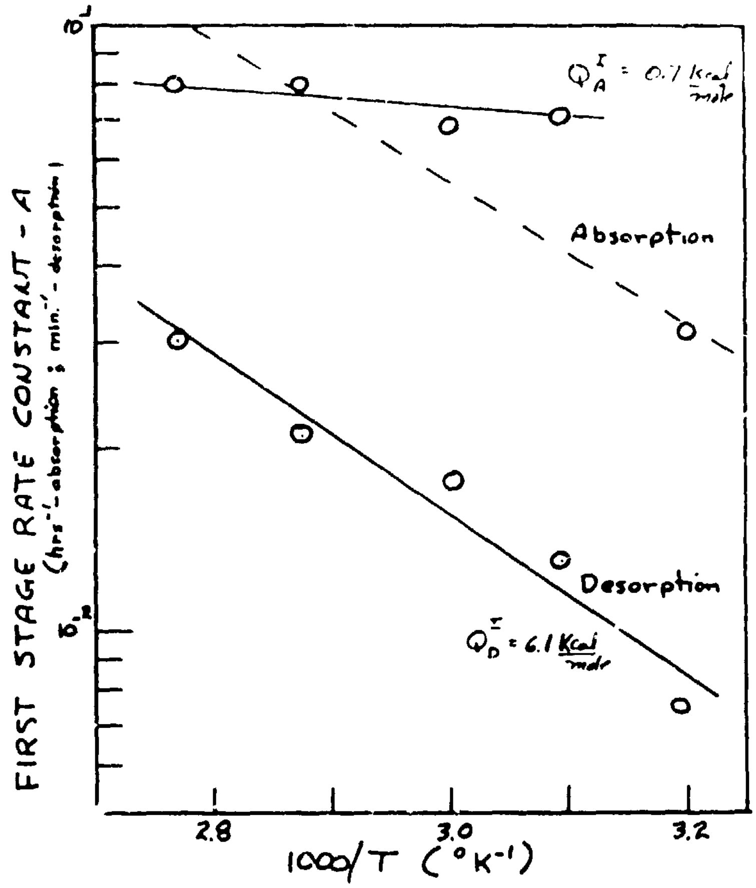
Time Dependence of Normalized Weight Loss in EVA Due to Water Desorption (40°C)



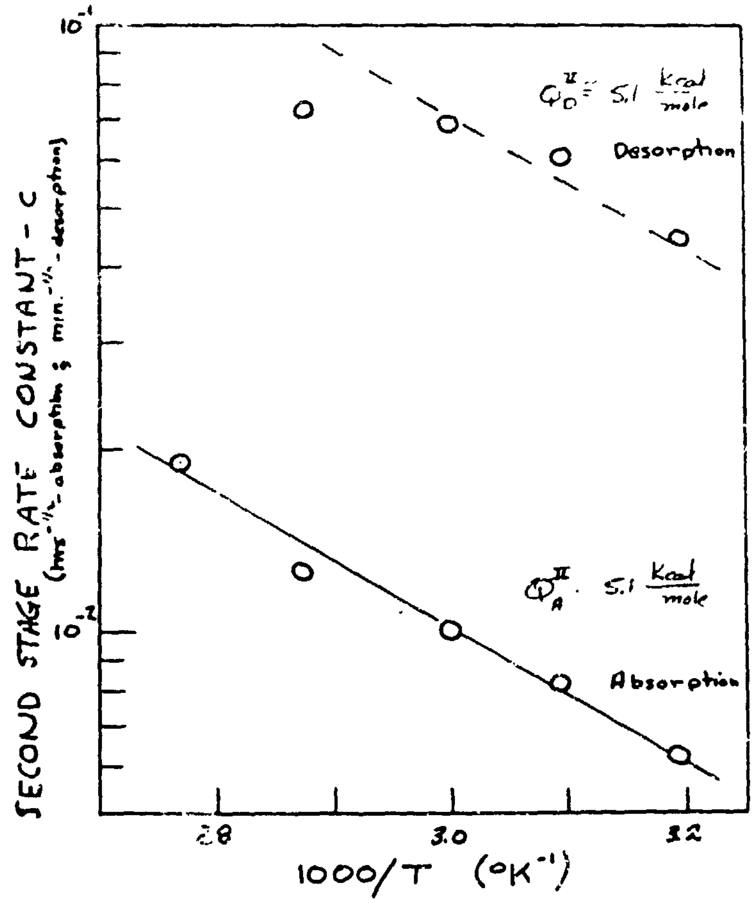
Characterizing Rate Constraints for Water Absorption and Desorption in EVA

	STAGE I		STAGE II	
	$\frac{W_t}{W_{oa}}$	At + B	$\frac{W_t}{W_{oa}}$	C[illegible]$^{1/2}$ + D
Temp.	A	B	C	D
Absorption				
	(hrs.$^{-1}$)		(hrs.$^{-1/2}$)	
88°C	.080	1.0	.0190	1.285
75°C	.080	1.0	.0125	1.4[illegible]0
60°C	.068	1.0	.010	1.570
50°C	.071	1.0	.0082	1.440
40°C	.031	1.0	.0062	1.[illegible]
Desorption				
	(min.$^{-1}$)		(min.$^{-1/2}$)	
88°C	.030	1.0	—	—
75°C	.021	1.0	.0723	1.[illegible]63
60°C	.0175	1.0	.0690	1.[illegible]70
50°C	.0130	1.0	.0605	1.[illegible]71
40°C	.0073	1.0	.441	1.[illegible]64

Temperature Dependence of the Rate Constant for First-Stage Water Absorption and Desorption in EVA



Temperature Dependence of the Rate Constant for the Second-Stage Water Absorption and Desorption in EVA



Activation Energies and Pre-Exponential Factors for Water Absorption and Desorption in EVA

STAGE I ← Surface Film

	Q^I (kcal/mole)	A_o (min.$^{-1}$)
Absorption	0.7 (=Q^I_A)	.0033 (0.2 hrs.$^{-1}$)
Desorption	6.1 (=Q^I_D)	167

STAGE II - Volume Diffusion

	Q^{II} (Kcal/mole)	Co (min $^{-\frac{1}{2}}$)
Absorption	5.1 (=Q^{II}_A)	3 (23 hrs. $^{-\frac{1}{2}}$)
Desorption	5.1 (=Q^{II}_D)	159

EVA Water Absorption Model

SEQUENTIAL REACTION STEPS:

STEP 1: CONDENSATION OF ATMOSPHERIC WATER AS A MONOLAYER ON SURFACE

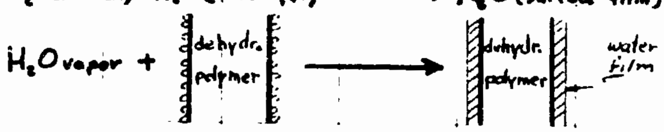
REACTION: H_2O (in atmosphere) ⟶ H_2O (monolayer on surface)

SCHEMATIC ILLUSTRATION:

STEP 2a: CONDENSATION OF SUCCESSIVE MONOLAYERS TO FORM A SURFACE FILM

REACTION: H_2O (in atm.) + H_2O (monolayer) ⟶ H_2O (surface film)

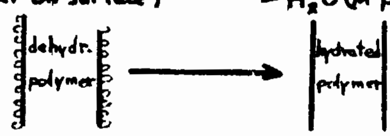
SCHEMATIC ILLUSTRATION:



STEP 2b: DIFFUSION OF MONOLAYER INTO POLYMER

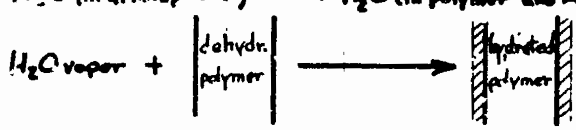
REACTION: H_2O (monolayer on surface) ⟶ H_2O (in polymer)

SCHEMATIC ILLUSTRATION:



OVERALL REACTION:

H_2O (in atmosphere) ⟶ H_2O (in polymer and in surface film)



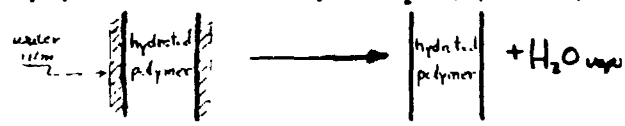
EVA Water Desorption Model

SEQUENTIAL REACTION STEPS:

STEP 1: EVAPORATION OF THE ADSORBED WATER FILM ON SURFACE

REACTION: H_2O (in polymer and in surface film) → H_2O (in polymer) + H_2O (in vapo

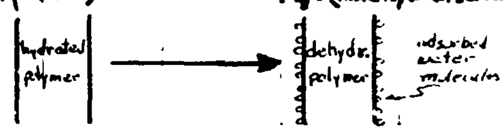
SCHEMATIC ILLUSTRATION:



STEP 2: VOLUME DIFFUSION OF WATER OUT OF POLYMER TO SURFACE

REACTION: H_2O (in polymer) → H_2O (monolayer on surface)

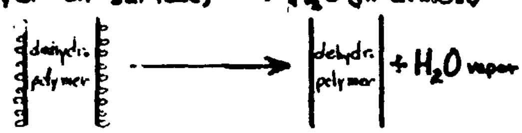
SCHEMATIC ILLUSTRATION:



STEP 3: EVAPORATION OF WATER MONOLAYER ON SURFACE

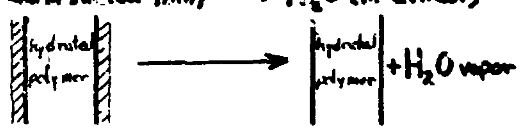
REACTION: H_2O (monolayer on surface) → H_2O (in atmos.)

SCHEMATIC ILLUSTRATION:



OVERALL REACTION:

H_2O (in polymer and in surface film) → H_2O (in atmos.)



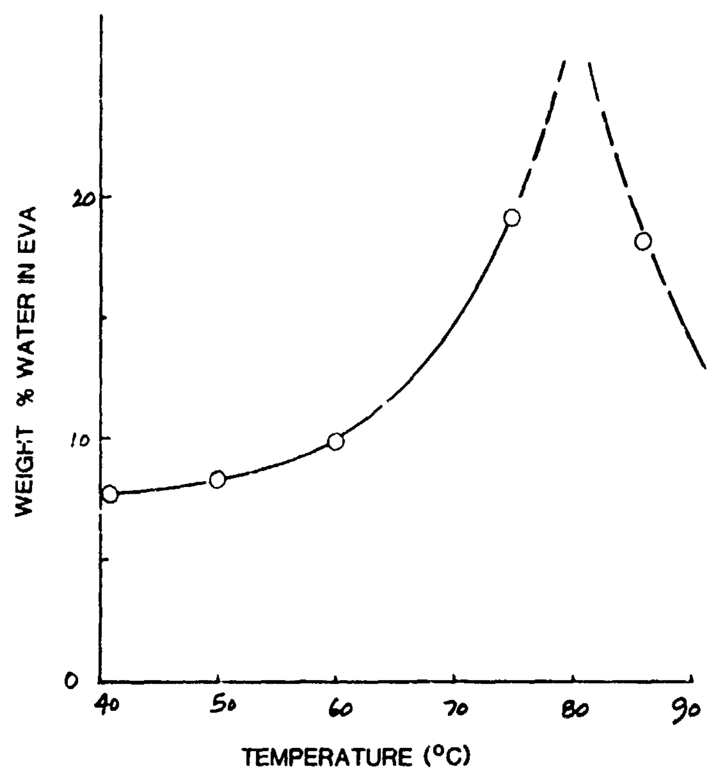
Weight-Gain Characteristics of EVA in Water Absorption Due to Surface-Film Formation and Volume Absorption

Temperature	W_∞ / W_{oa}: Total Normalized Weight Gain	W_∞: total weight gain per gram EVA (gms)	W_s/W_{oa}: Total Normalized Weight Gain Due to Surface Film Formation (gms)	W_s: Weight Gain per Gram EVA due to Surface film Formation (gms)	W_v: Weight Gain per Gram EVA Due to Volume Absorption (gms)	$W_{\%}$: Weight Percent Solubility of water In EVA (%)
88 °C	[illegible]	[illegible]	1.285*	.285	.195	[illegible]
75 °C	[illegible]	[illegible]	1.460*	.460	.240	19.3
60 °C	[illegible]	[illegible]	1.570*	.570	.110	[illegible]
50 °C	1.58•	.58	1.490*	[illegible]	.040	8.2
40 °C	1.42•	.42	1.335*	.335	.085	[illegible]

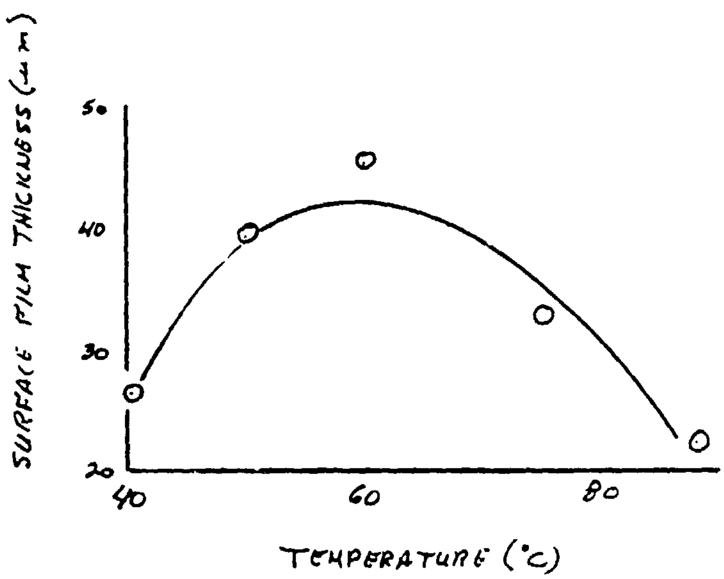
• Determined from data in Table I

* Taken from extrapolated D intercept values in Table II

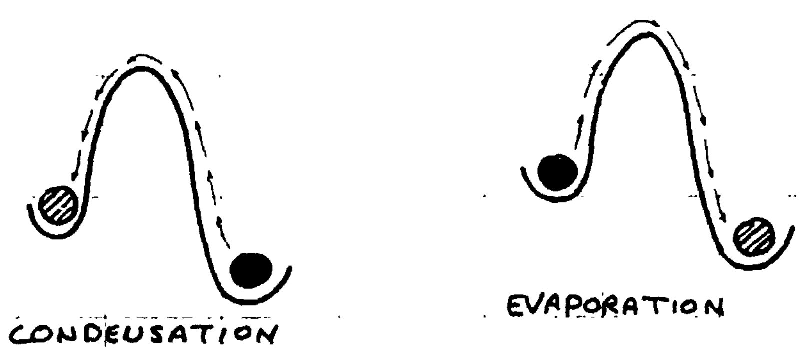
Solubility of H_2O in EVA as a Function of Temperature



Equilibrium Thickness of Absorbed Water Film on EVA as a Function of Temperature



Energy Barrier for Condensation and Evaporation During the Stage I Kinetic Response in Water Absorption and Desorption on EVA

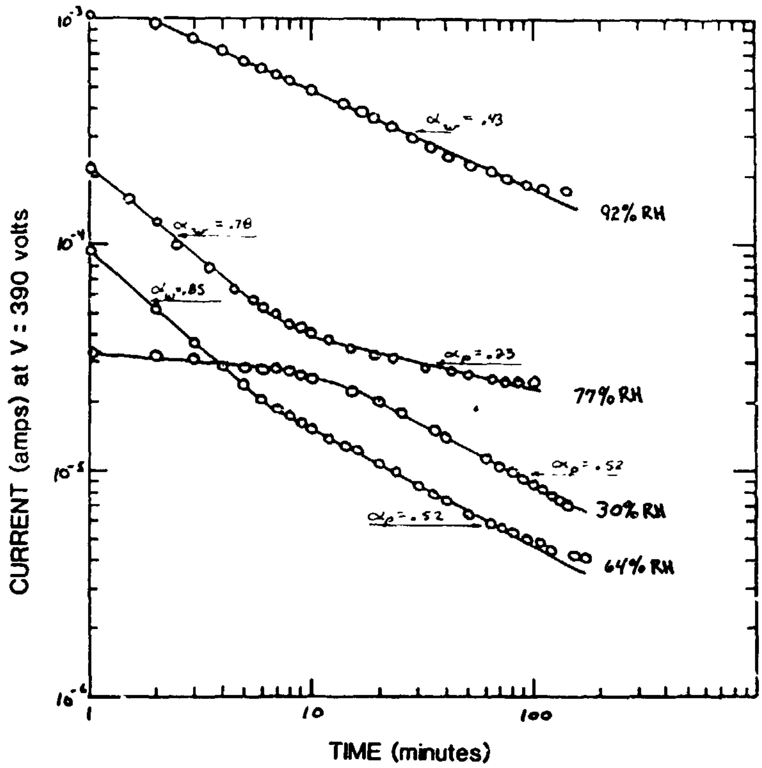


Water Interaction Comparison of EVA and PVB

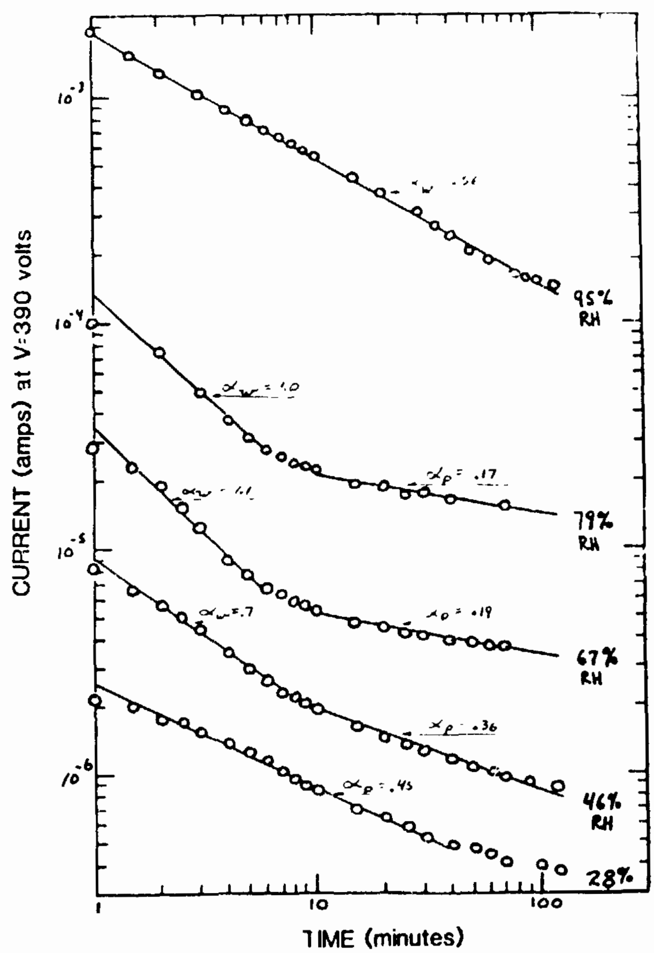
	PVB	EVA
WATER SOLUBILITY AT 60°C (w/o)	38	10
ACTIVATION ENERGIES (Kcal/mole)		
ABSORPTION		
STAGE I	4.2	0.7
STAGE II	6.3	5.1
DESORPTION		
STAGE I	16	6.1
STAGE II	7.1	5.1
STAGE I ABSORPTION RATE OF WATER PER GRAM OF POLYMER AT 25°C (gms/hr)	$2.5(10^{-4})$	$6.1(10^{-2})$
STAGE I DESORPTION RATE OF WATER PER GRAM OF POLYMER AT 25°C (gms/hr)	$9.9(10^{-2})$	$5.5(10^{-3})$

HUMIDITY DEPENDENCE OF THE ELECTRICAL PROPERTIES OF EVA AND PVB

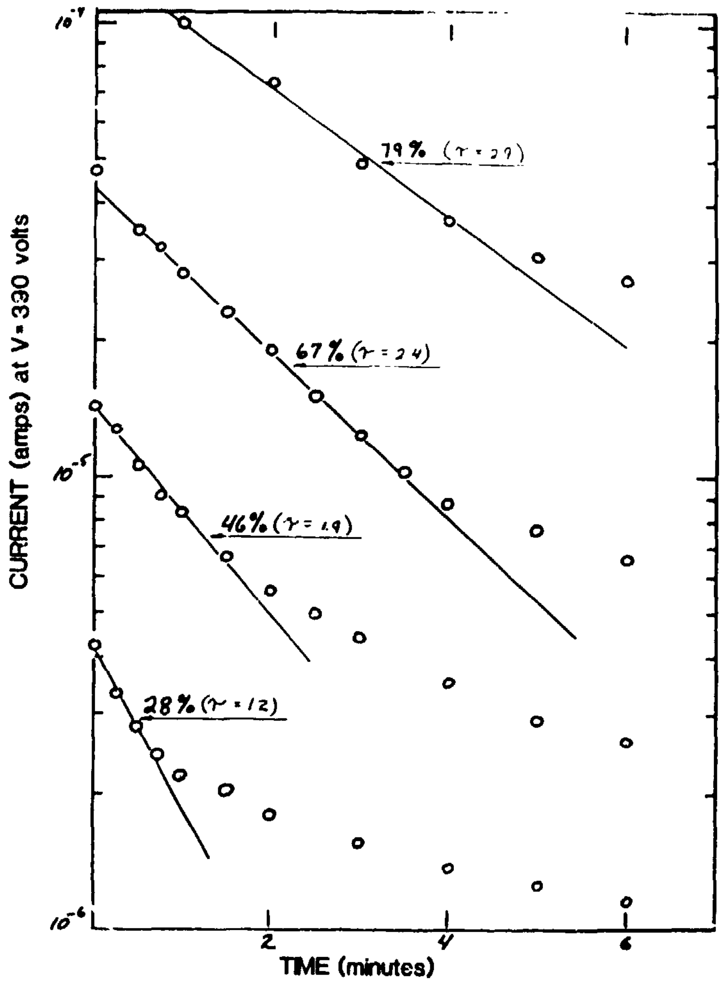
Current Response to a 390-V Step Voltage for PVB (80°C)



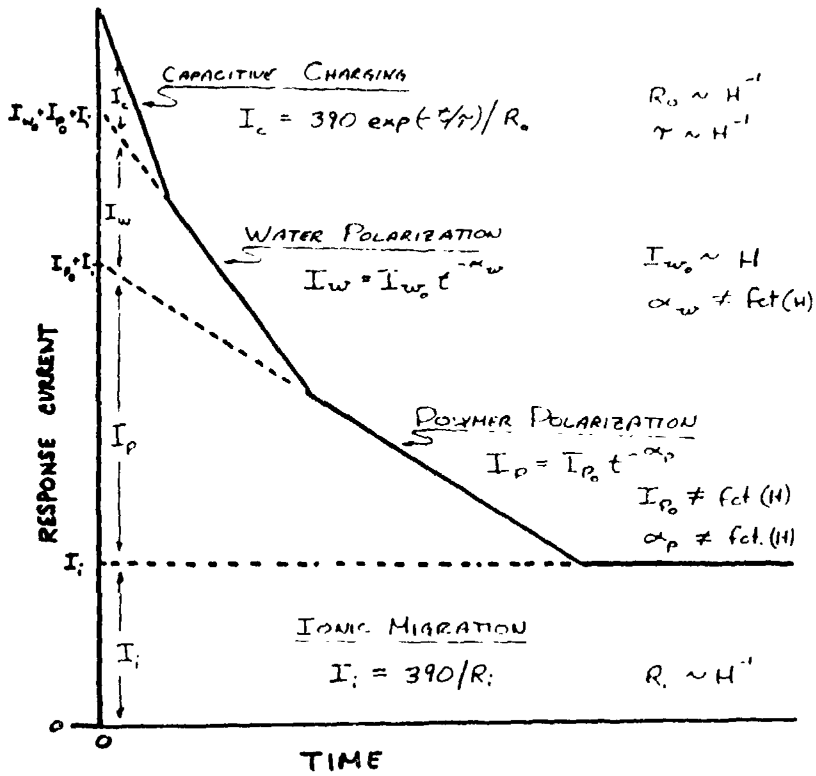
Current Response to a 390-V Step Voltage for PVB (68°C)



Initial Transient Behavior for the Current Response to a 390-V Step Voltage for PVB (68°C)



Proposed Current Response to a Step Voltage



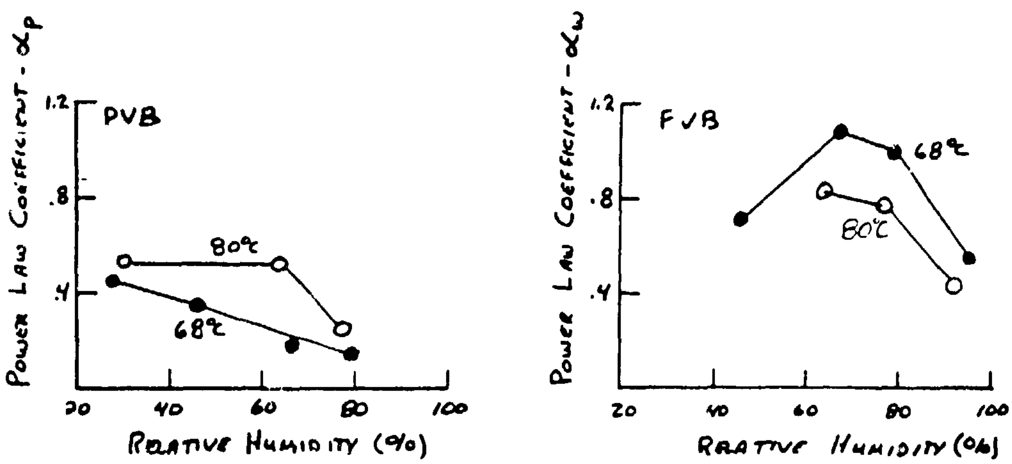
Current Response Parameters for PVB (80°C)

RELATIVE HUMIDITY (%)	TIME RANGE (min.)	CURRENT COMPONENTS	TIME DEPENDENCE $I = A\,t^{-\alpha}$: A ($= I_w + I_p + I_i$)	α	I_{w_o}	I_{p_o}	I_i
92	$0 < t < 100$	$I_w + I_i$	1.3(10^{-3})	.43($= \alpha_w$)	1.2(10^{-3})	–	–
	$t > 100$	I_i	–	–	–	–	1.7(10^{-4})
77	$0 < t < 10$	$I_w + I_p + I_i$	2.1(10^{-4})	.78($= \alpha_w$)	1.5(10^{-4})	–	–
	$10 < t < 100$	$I_p + I_i$	6.5(10^{-5})	.23($= \alpha_p$)	–	4.1(10^{-5})	–
	$t > 100$	I_i	–	–	–	–	2.5(10^{-5})
64	$0 < t < 7$	$I_w + I_p + I_i$	9.5(10^{-5})	.85($= \alpha_w$)	4(10^{-5})	–	–
	$7 < t < 100$	$I_p + I_i$	5.0(10^{-5})	.52($= \alpha_p$)	–	4.6(10^{-5})	–
	$t > 100$	I_i	–	–	–	–	4(10^{-6})
30	$20 < t < 100$	$I_p + I_i$	97(10^{-9})	.52($= \alpha_p$)	–	–	–
	$t > 100$	I_i	–	–	–	–	7(10^{-8})

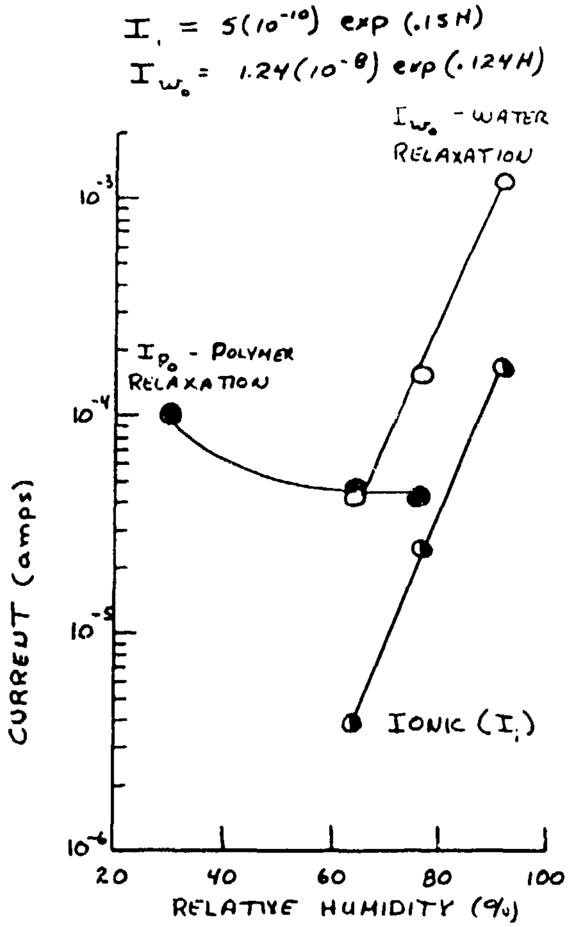
Current Response Parameters for PVB (68°C)

RELATIVE HUMIDITY (%)	TIME RANGE (min)	CURRENT COMPONENTS	I_i (amps)	$R_i = 390/I_i$ (Ω)	TIME DEPENDENCE: $I = At^{-\alpha}$ — A (amps)	α	$I = [390/R_o][\exp(-t/\tau)]$ — 390/R(ohm)	R_o(Ω)	τ(min)
95	0<t<100	I_w+I_i			1.9(10^-1)	.56(=α_w)	—	—	—
	t>100	I_i	2(10^-4)	19(10^5)					
79	0<t<4	$I_c+I_w+I_p+I_i$			—	—	14(10^-4)	28(10^4)	29
	2<t<6	$I_w+I_p+I_i$			1.4(10^-4)	1.0(=α_w)	—	—	—
	10<t<100	I_p+I_i			3.2(10^-5)	0.17(=α_p)	—	—	—
	t>100	I_i	1.5(10^-5)	2.6(10^7)					
67	0<t<4	$I_c+I_w+I_p+I_i$			—	—	4.3(10^-5)	9.0(10^6)	24
	2<t<6	$I_w+I_p+I_i$			5.9(10^-5)	1.1(=α_w)	—	—	—
	10<t<100	I_p+I_i			8.0(10^-6)	0.19(=α_p)	—	—	—
	t>100	I_i	3(10^-8)	1.3(10^9)					
46	0<t<2	$I_c+I_w+I_p+I_i$			—	—	14(10^-5)	28(10^7)	19
	2<t<10	$I_w+I_p+I_i$			9.4(10^-6)	0.72(=α_w)	—	—	—
	10<t<100	I_p+I_i			4.5(10^-6)	0.36(=α_p)	—	—	—
	t>100	I_i	8(10^-9)	4.9(10^8)					
28	0<t<1	$I_c+I_p+I_i$			—	—	4.2(10^-6)	9.2(10^7)	12
	2<t<50	I_p+I_i			2.4(10^-6)	0.45(=α_p)	—	—	—
	t>50	I_i	4(10^-9)	9.8(10^8)					

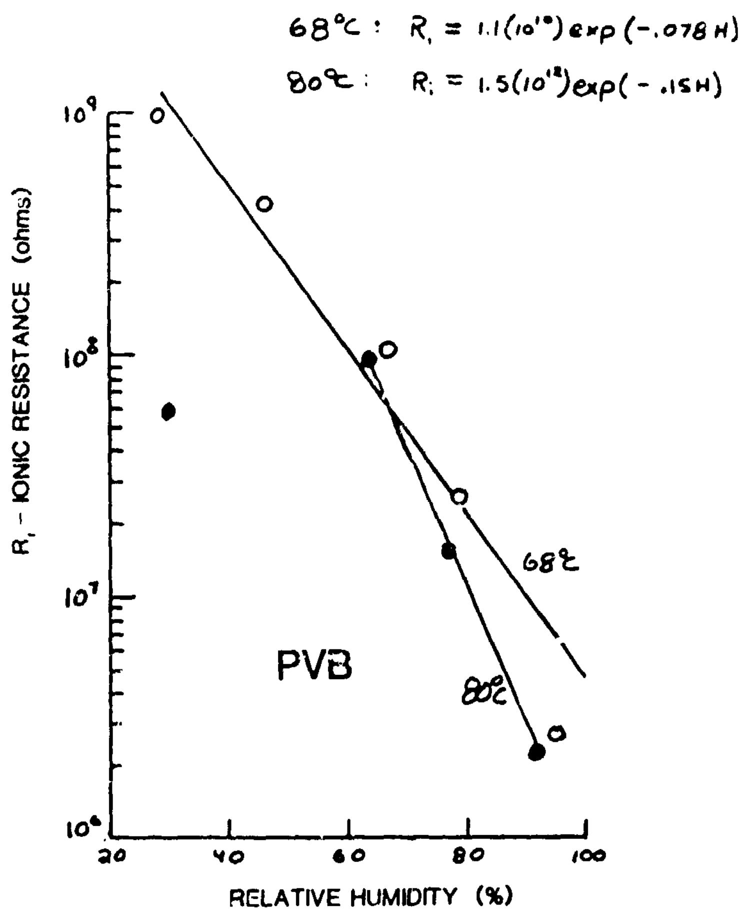
Dependence on Relative Humidity of the Current Response Coefficients κ_p and κ_w



Ionic and Polarization Components of the Response Current vs RH (PVB at 80°C)

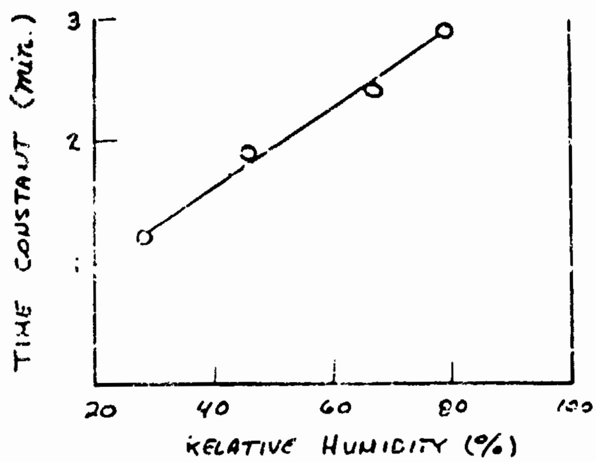


Ionic Resistance vs Relative Humidity (80°C and 68°C)

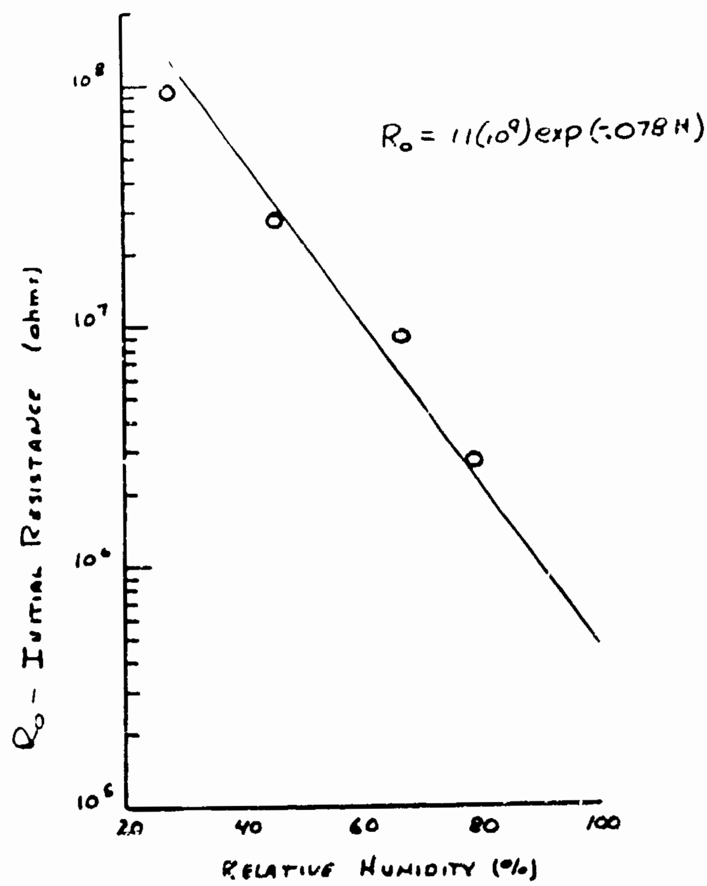


Time Constants vs Relative Humidity for PVB (68°C)

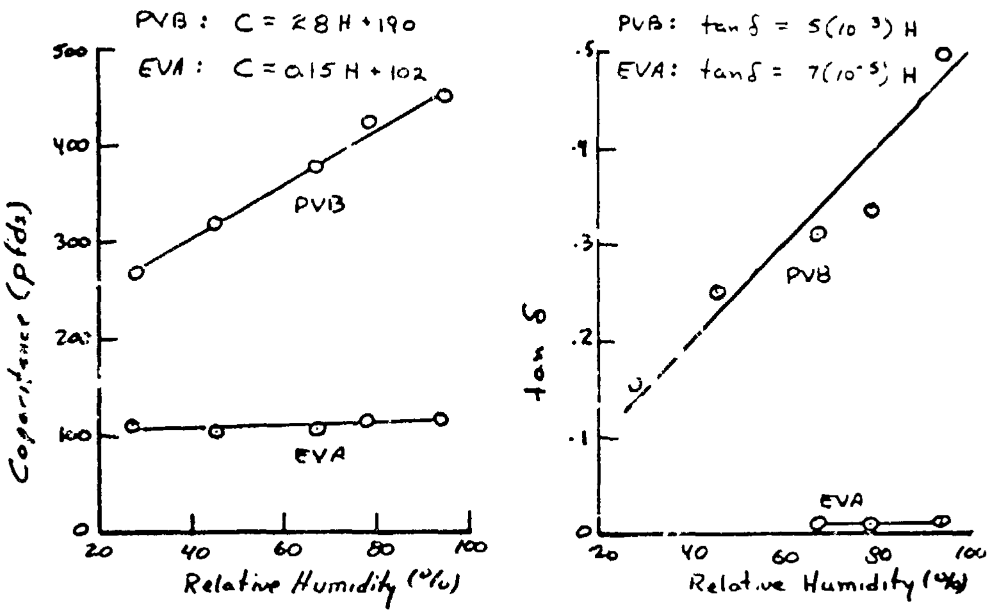
$\tau = .033H + 0.3$



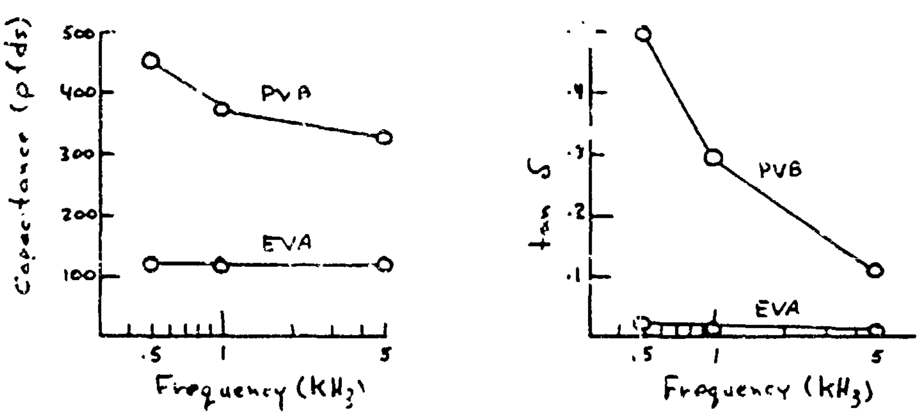
Humidity Dependence of the Initial Resistance for PVB (68°C)



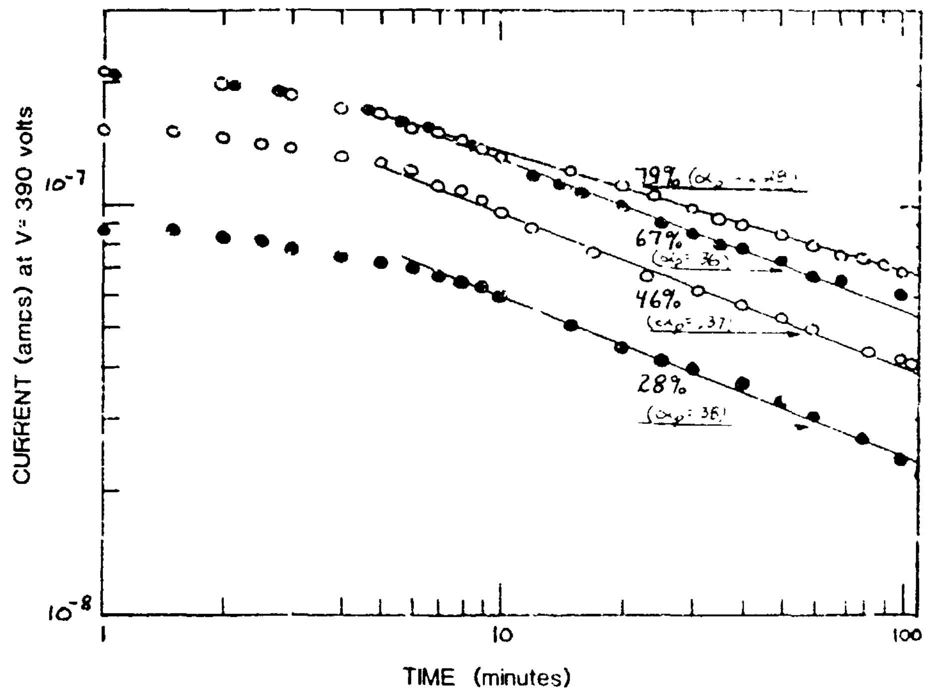
Capacitance and (tan δ) vs RH (500 Hz and 68°C)



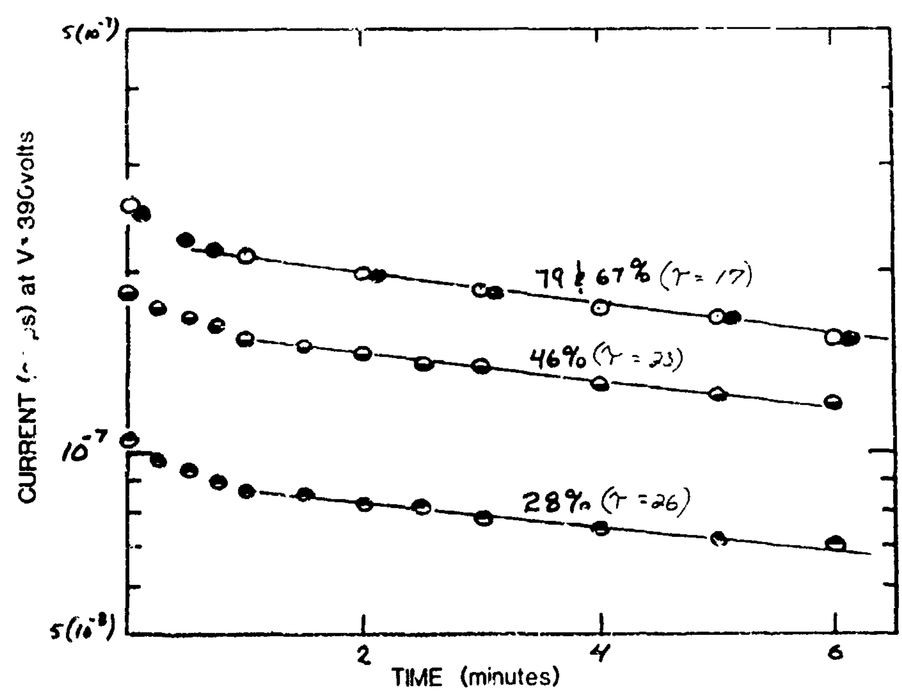
Capacitance and (tan δ) vs Frequency (68°C/95% RH)



Current Response to a 390-V Step Voltage for EVA at Various RH (%) Levels (68°C)



Initial Transient Current Response to a 390-V Step Voltage for EVA (68°C)



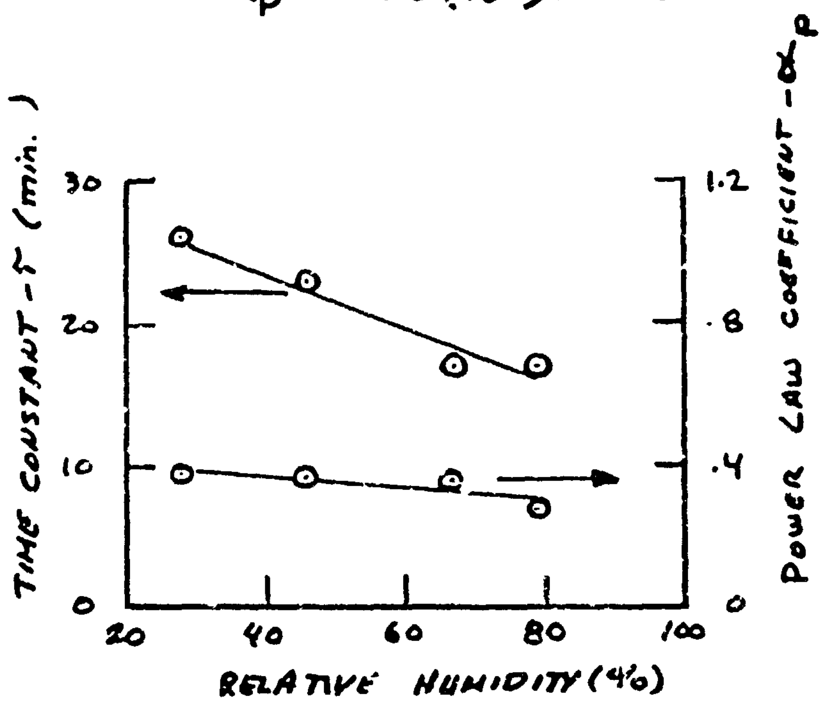
Current Response Parameters for EVA (68°C)

RELATIVE HUMIDITY (%)	TIME RANGE (min)	CURRENT COMPONENTS	I_i (amps)	$R_i = 390/I_i$ (Ω)	TIME DEPENDENCE: $I = At^{-\alpha}$ — A (amps)	α_p	DEPENDENCE: $I = [390/R_o][\exp(-t/\tau)]$ — $390/R_o$	R_o (Ω)	τ (min)
79	1<t<6	$I_c+I_p+I_i$			—	—	2.2(10^{-7})	18(10^{9})	17
	6<t<100	I_p+I_i			2.6(10^{-7})	.28	—	—	—
	t>100	I_i	~7(10^{-9})	~55(10^{9})					
57	1<t<6	$I_c+I_p+I_i$			—	—	2.2(10^{-7})	18(10^{9})	17
	6<t<100	I_p+I_i			3.0(10^{-7})	.36	—	—	—
	t>100	I_i	~6(10^{-8})	6.5(10^{9})					
46	1<t<6	$I_c+I_p+I_i$			—	—	1.6(10^{-7})	24(10^{9})	23
	6<t<100	I_p+I_i			2.3(10^{-7})	.37	—	—	—
	t>100	I_i	4.2(10^{-9})	92(10^{9})					
28	1<t<6	$I_c+I_p+I_i$			—	—	8.8(10^{-8})	44(10^{9})	26
	6<t<100	I_p+I_i			1.5(10^{-7})	.38	—	—	—
	t>100	I_i	~25(10^{-9})						

Power-Law Coefficient κ and Time Constant τ vs RH for Current Response of EVA to a 390-V Step Voltage (68°C)

$$\tau = -.19H + 31$$

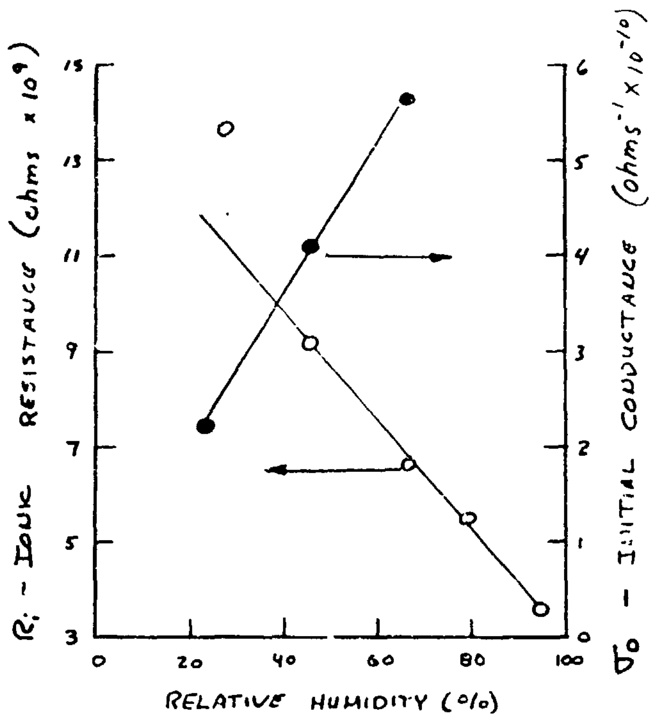
$$\alpha_p = -1.5(10^{-3})H + .43$$



Ionic Resistance and Initial Conductance vs Relative Humidity for EVA (68°C)

$$R_i = -1.13(10^{8})H + 1.4(10^{10})$$

$$R_o = \frac{1}{\sigma_o} = \frac{1}{8(10^{-12})H + 4(10^{-11})}$$



Measure and Calculated Time Constants for Capacitive Charging of EVA and PVB (68°C)

Humidity %	Time Constants (min.) PVB measured	PVB calculated	EVA measured	EVA calculated
79	2.9	$1.0(10^{-5})$	17	$3.5(10^{-3})$
67	2.4	$5.0(10^{-5})$	17	$3.5(10^{-3})$
46	1.9	$1.4(10^{-4})$	23	$4.2(10^{-3})$
28	1.2	$4.0(10^{-4})$	26	$7.9(10^{-3})$

Humidity Dependencies of Selected Properties of PVB and EVA (68°C)

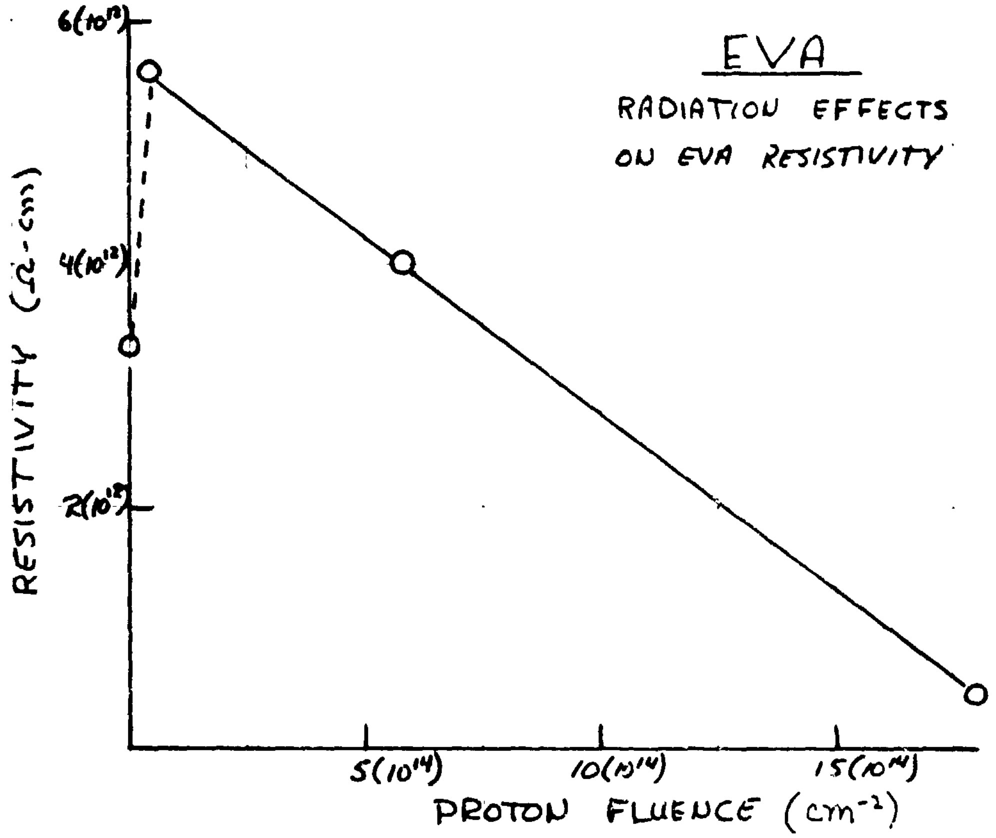
Property	Expected Dependency	Experimentally Observed Dependencies: PVB	Experimentally Observed Dependencies: EVA
$R_0(\Omega)$	$=[\gamma H + \beta]$	$=1.1(10^{9})\exp(-.078H)$	$=[8(10^{-12})H + 4(10^{-11})]^{-1}$
$R_1(\Omega)$	$=[\gamma H + \beta]^{-1}$	$=1.1(10^{10})\exp(-.078H)$	$=-1.13(10^{8})H + 1.4(10^{10})$
α_w	$\neq fct(H)$	?	—
α_p	$\neq fct(H)$	$=-6.4(10^{-3})H + .64$	$=-1.5(10^{-3})H + .43$
τ (min)	$=[\delta H + \eta]/[\gamma H + \beta]$	$=.033H + 0.3$	$=-.19H + 31$
C (pfds)	$=\delta H + \eta$	$=2.8H + 190$	$=0.15H + 102$
$\tan\delta$	$=\delta H + \eta$	$=5(10^{-3})H$	$=.7(10^{-4})H$

Effects of Plasticizer on the Resistivity of PVB

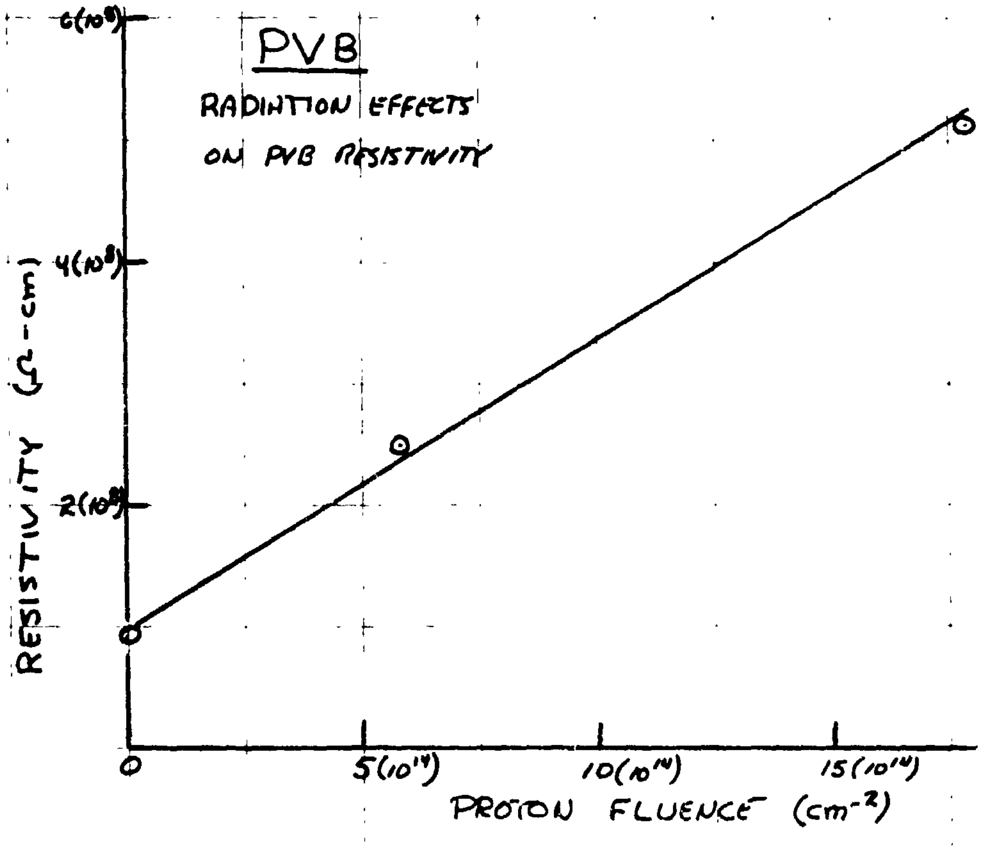
PVB	RESISITIVITY (Ω -cm)
UNPLASTICIZED	$3(10^{14})$
PHTHALATE PLASTICIZED	$5(10^{9})$
PHTHALATE REMOVED	$6(10^{14})$

RADIATION EFFECTS IN PVB and EVA

Radiation Effects on EVA Resistivity



Radiation Effects on PVB Resistivity



Conclusions

I. WATER ABSORPTION EXPERIMENTS

- FAST WATER DESORPTION KINETICS IN PVB AND EVA
- SLOW WATER ABSORPTION KINETICS IN PVB AND EVA
- WATER ABSORBED IN PVB IS LARGE
- WATER ABSORBED IN EVA IS SMALL

II. ELECTRICAL PROPERTIES OF PVB AND EVA

- IONIC RESISTANCE : $Ri^{PVB} < Ri^{EVA}$ 10^{2}
- CAPACITANCE : $C^{PVB} > C^{EVA}$ 10^{1}
- LOSS FACTOR : $\tan\delta^{PVB} > \tan\delta^{EVA}$ $10^{[illegible]}$
- HUMIDITY DEPENDENCE : PVB > EVA
- WATER DIPOLE EFFECTS IN PVB
- NO WATER DIPOLE EFFECTS IN EVA

III. PLASTICIZER EFFECTS ON IONIC RESISTANCE OF PVB

- Ri UNPLASTICIZED > Ri PLASTICIZED 10^{5}

IV. IONIZING RADIATION EFFECTS ON RESISTANCE OF PVB AND EVA

- PVB : Ri ↑ AS DOSE ↑
- EVA : Ri ↓ AS DOSE ↑

Future Work

- TEMPERATURE DEPENDENCE OF ELECTRICAL PROPERTIES OF EVA AND PVB
- UV LIGHT EFFECTS ON THE ELECTRICAL PROPERTIES OF EVA AND PVB AS A FUNCTION OF HUMIDITY AND TEMPERATURE
- EFFECT ON COMPOUNDING AGENTS ON ELECTRICAL PROPERTIES OF PVB AND EVA
- CORROSION EFFECTS IN SOLAR CELL MATERIALS
- THEORETICAL MODELS FOR HUMIDITY DEPENDENCY OF ELECTRICAL PROPERTIES