PHOTOTHERMAL CHARACTERIZATION OF POLYMERIC ENCAPSULATION MATERIAL

JET PROPULSION LABORATORY

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Major Modes of Degradation

- LOSS OF STABILIZERS
- PHOTOTHERMAL OXIDATION

Objectives

- STUDY MECHANISMS OF DEGRADATION
- DETERMINE MATERIAL RESPONSE TO DEGRADATION
- RANK AND SCREEN MATERIALS

In: *Proceedings of the Flat-Plate Solar Array Project Research Forum on Quantifying Degradation* (December 6-8, 1982, Williamsburg, Virginia), JPL Publication 83-52, JPL Document 5101-231, DOE/JPL-1012-89, Jet Propulsion Laboratory, Pasadena, California, June 1, 1983, pp. 303-336.

Materials Tested

- POTTANTS
  - ETHYLENE VINYL ACETATE (EVA, SPRINGBORN A9918)
  - POLY VINYL BUTYRAL (PVB, MONSANTO SR-11)
  - ETHLENE METHYL ACRYLATE (EMA, SPRINGBORN A13404)
  - ALIPHATIC POLYURETHANE (PU, DEVELOPMENT ASSOCIATES INC. Z-2591)
  - POLY-n-BUTYL ACRYLATE (PnBA, SPRINGBORN A13870)
  - SILICONE (RTV, GENERAL ELECTRIC RTV615)
- FRONT COVER MATERIALS
  - KORAD (XCEL 212R)
  - TEDLAR (DUPONT, 100 BG 30 UT)
  - ACRYLAR (3M-PMMA, X-22416 AND X-22417)
  - UV SCREENING ACRYLIC FILM (JPL DEVELOPED)

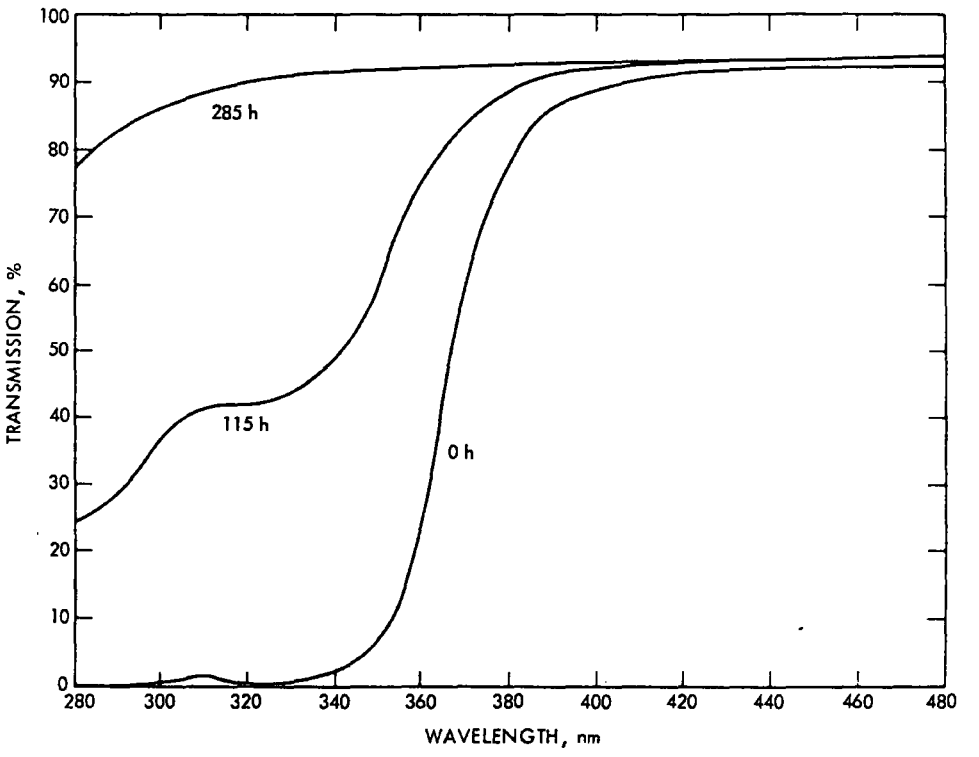
Controlled Environmental Reactor (CER)

- HIGH UV ACCELERATION
- HIGH TEMPERATURE CAPABILITY
- PRECISE TEMPERATURE CONTROL
- SIMULATED RAIN AND FOG
- OXYGEN AND NITROGEN ENVIRONMENT
- LOW COST
- REAL TIME OUTDOOR VALIDATION

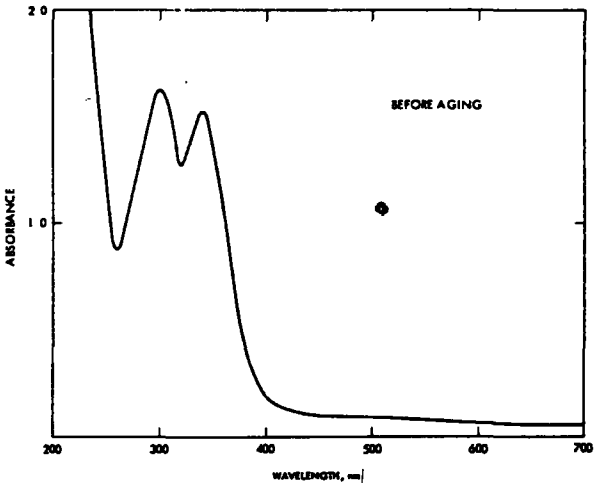
Problems Associated With UV-Screening Front-Cover Film

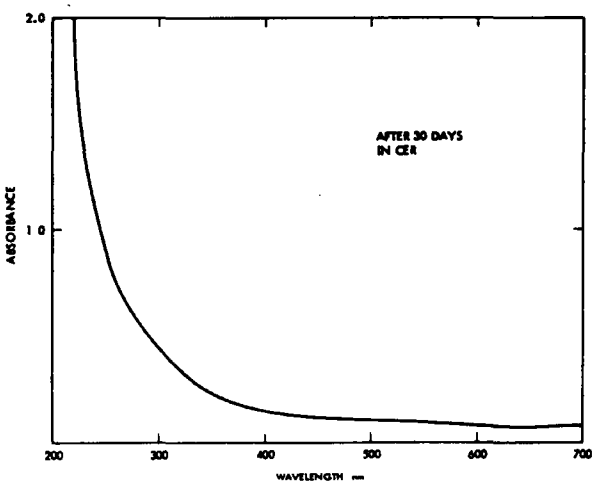
- LOSS OF UV-SCREENING CAPABILITY
- INDUCED DEGRADATION TO PARENT POLYMER VIA SENSITIZATION

UV-Vis Transmittance Spectra of Korad as a Function of Photothermal Aging in Air at 6 suns and 85°C

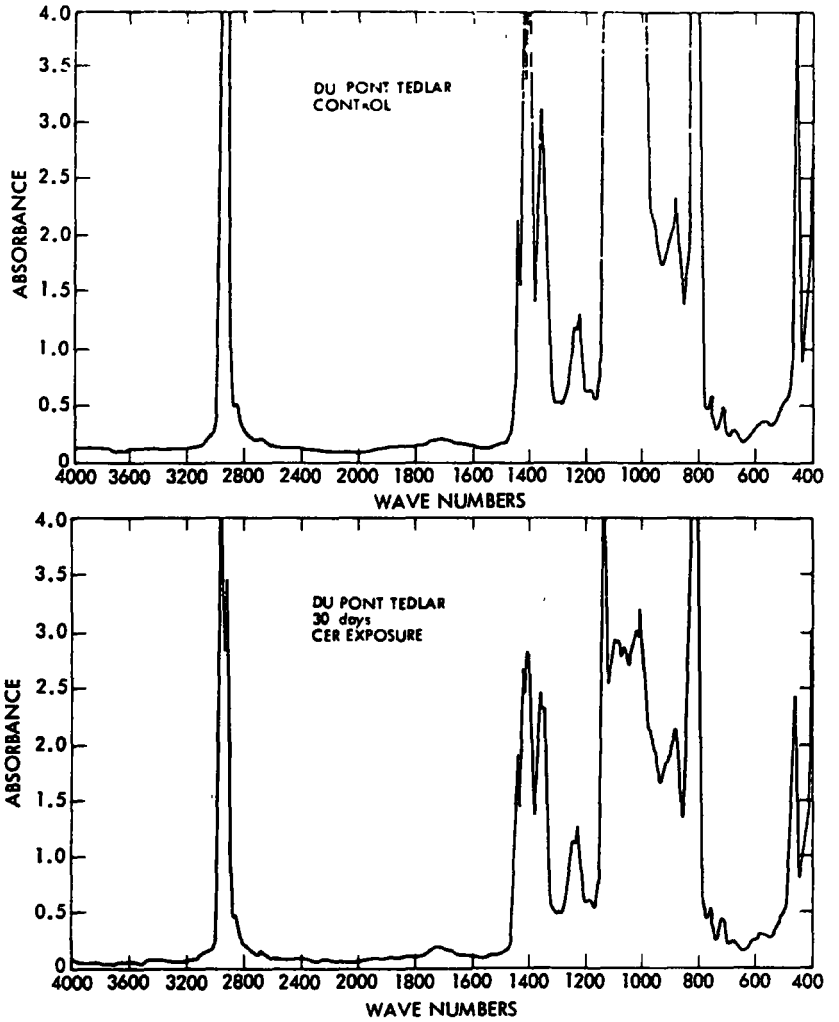


UV-Vis Absorbance Spectra of Tedlar UTB-100 Before and After 30 Days of Aging in CER

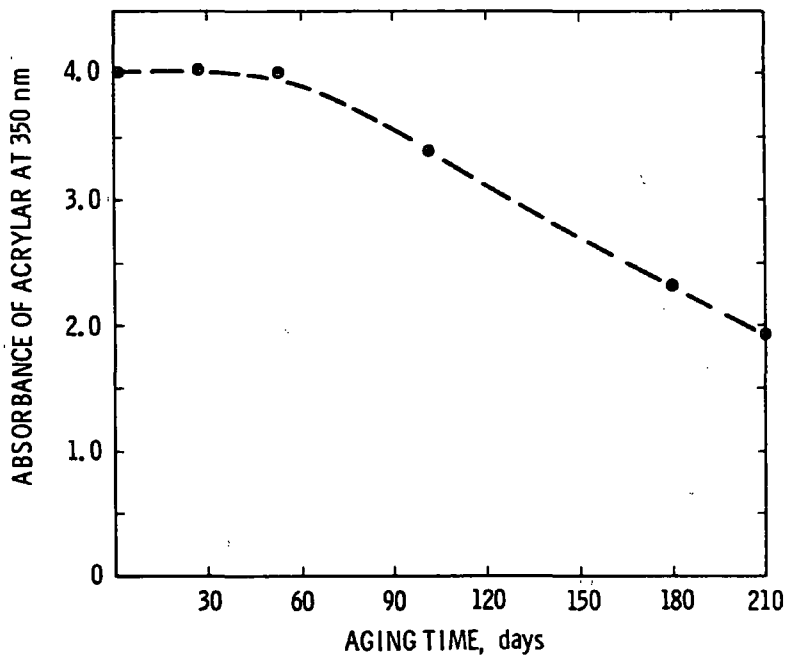




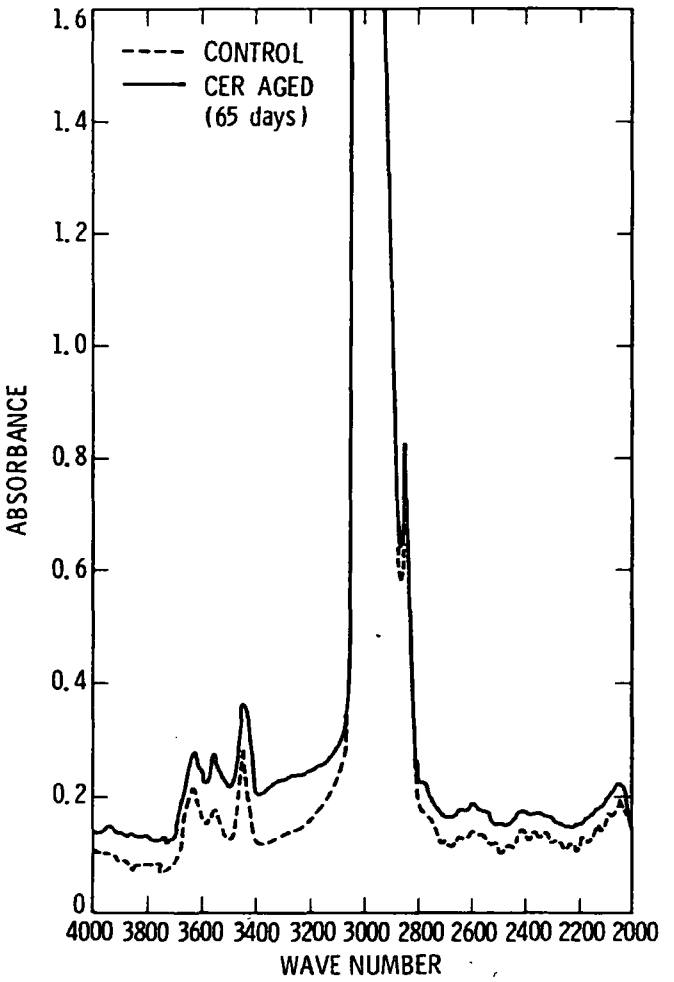
FT-IR Absorbance Spectra of Tedlar UTB-100 Before and After 30 Days of Aging in CER



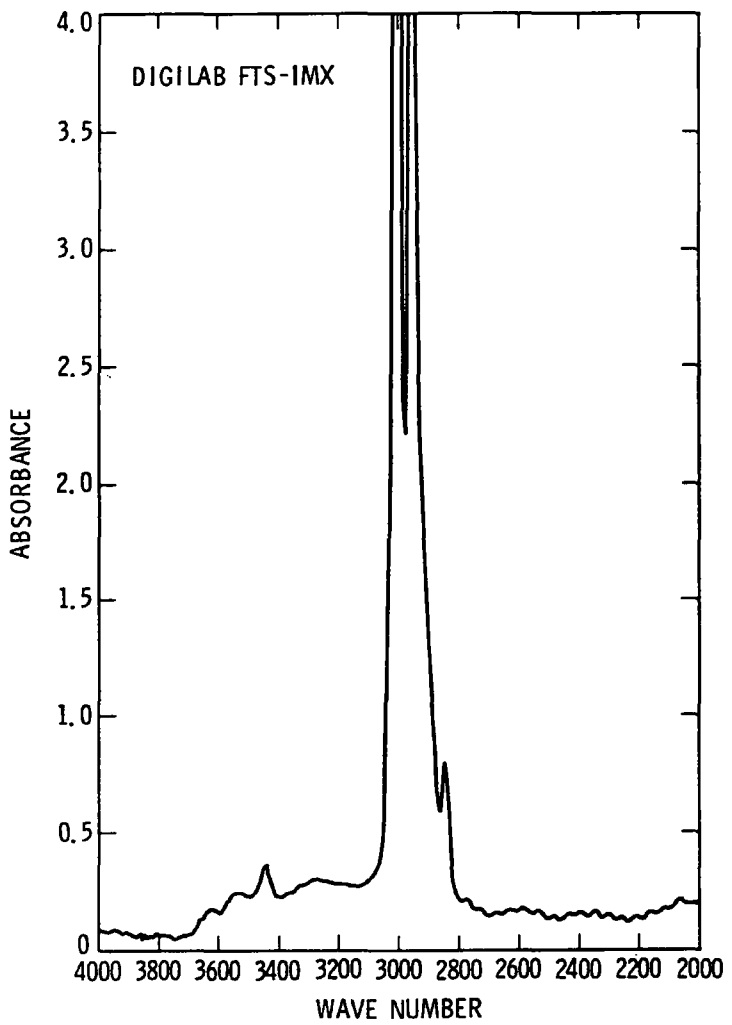
Aging Behavior of Acrylar in the CER



FT-IR Spectra of Acrylar



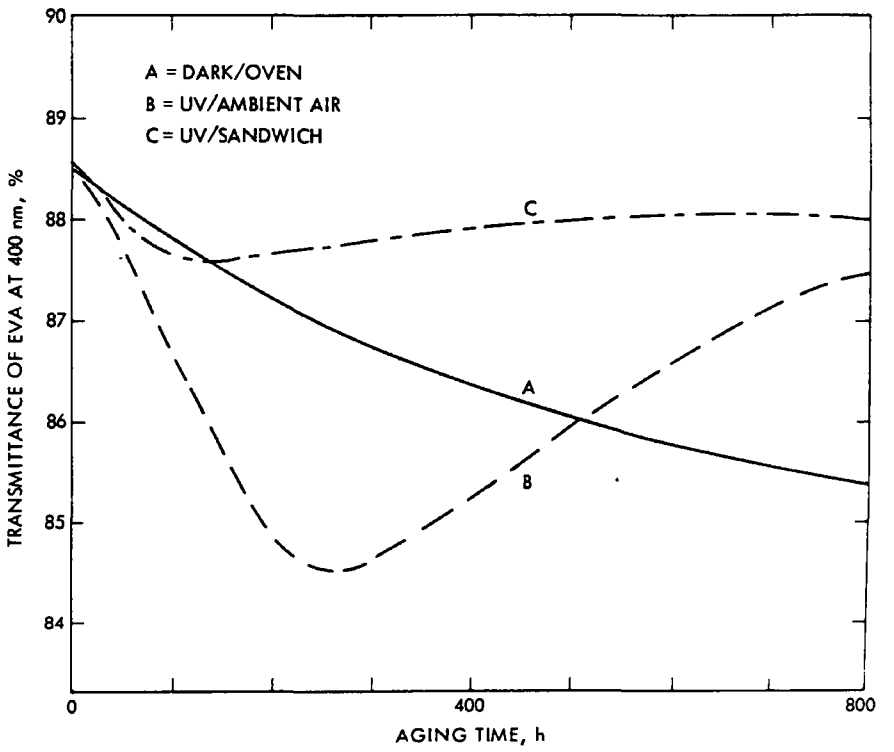
FT-IR Spectrum of Acrylar, CER-Aged 255 days



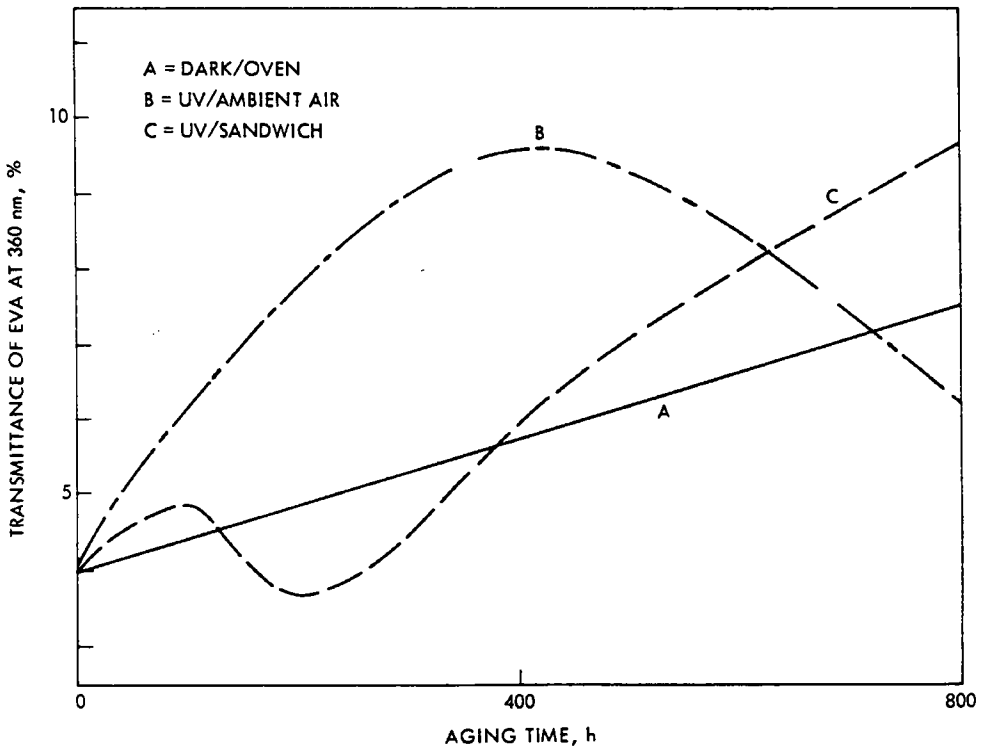
Properties Monitored

- OPTICAL TRANSMITTANCE
- WEIGHT LOSS
- SWELLING
- TENSILE MODULUS
- CHEMICAL CHANGES (FT-IR, HPLC, ETC.)

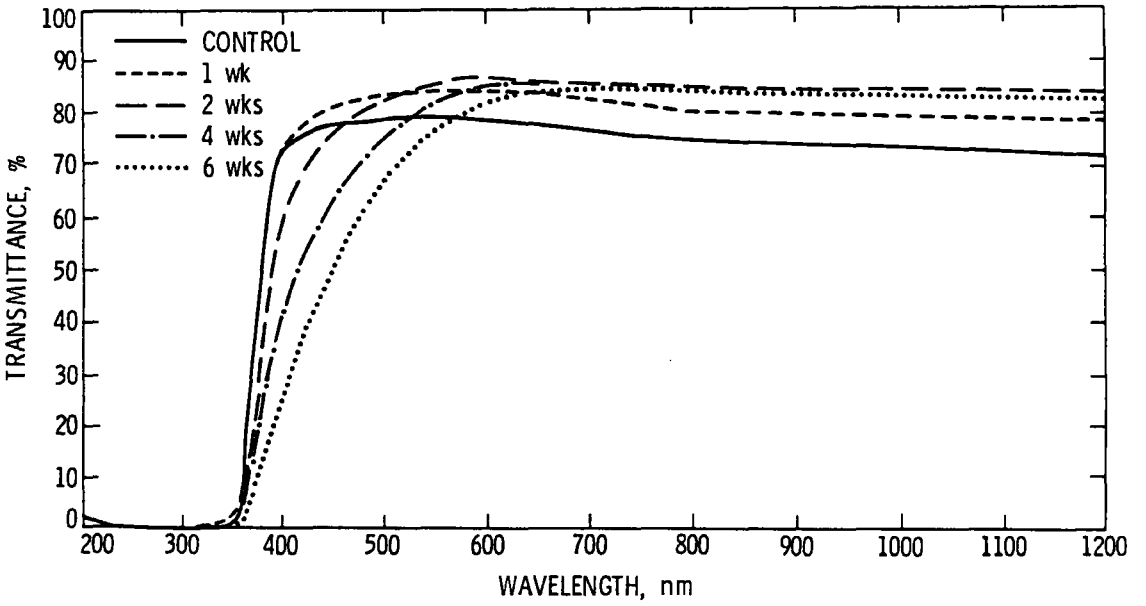
Change in Transmittance at 400 nm of A-9918 EVA Film as a Function of Photothermal Aging at 6 suns and 105°C



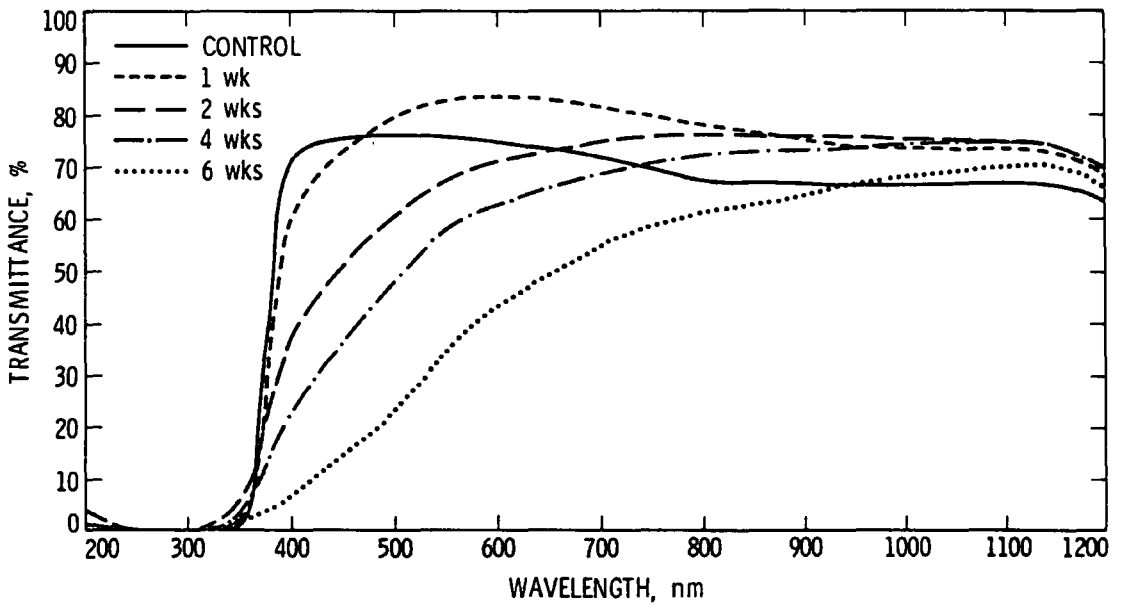
Change in Transmittance at 400 nm of A-9918 EVA Film as a Function of Photothermal Aging at 6 suns and 105°C



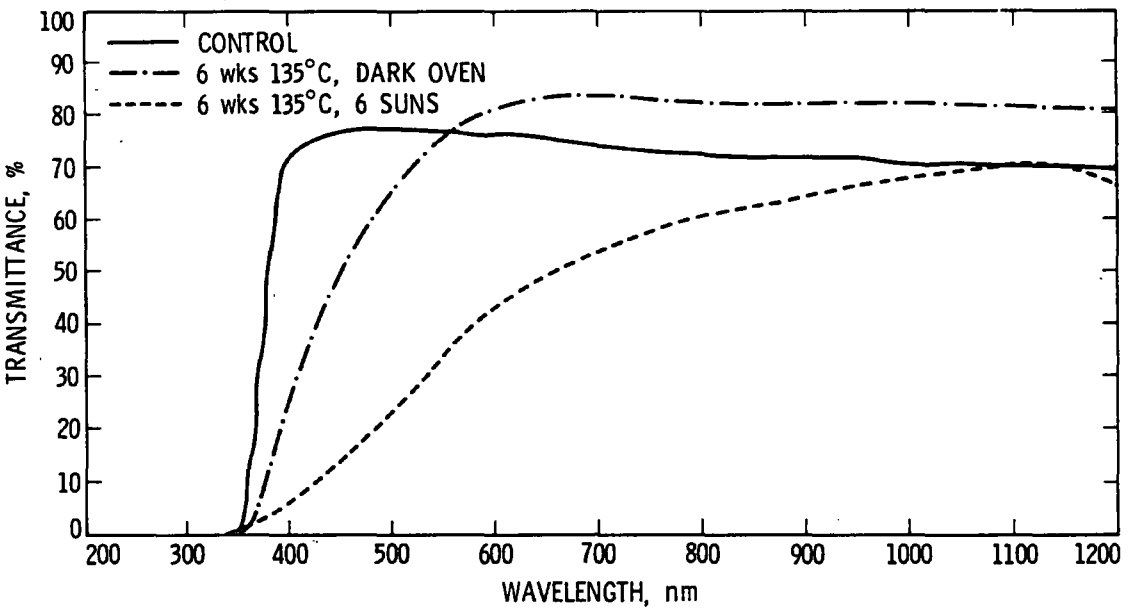
Transmittance Spectra of EVA-Sunadex (135°C, Dark Oven)



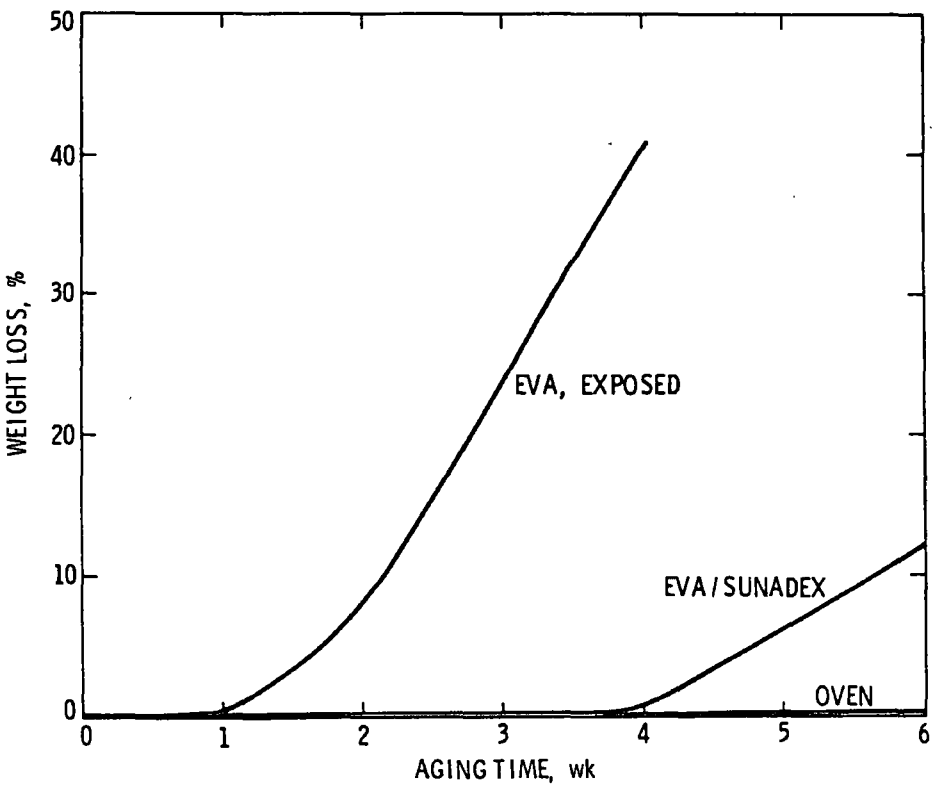
Transmittance Spectra of EVA-Sunadex (135°C, 6 suns)



Transmittance of EVA-Sunadex



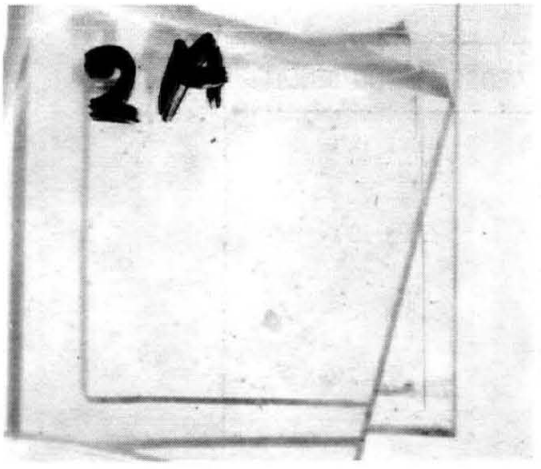
Weight Loss of EVA at 135°C



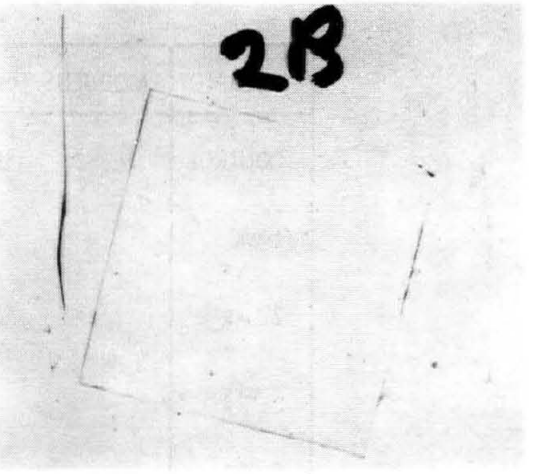
Modulus and Crosslinking Density of EVA as a Function of Photothermal Aging at 135°C and 6 suns

SAMPLE	MODULUS (psi, 5% STRAIN)	CROSSLINKING DENSITY
CONTROL	1015	5.6×10^{-6}
1 wk	580	7.1×10^{-6}
2 wks	595	33.8×10^{-6}
4 wks	661	72.8×10^{-6}
6 wks	864	98×10^{-6}

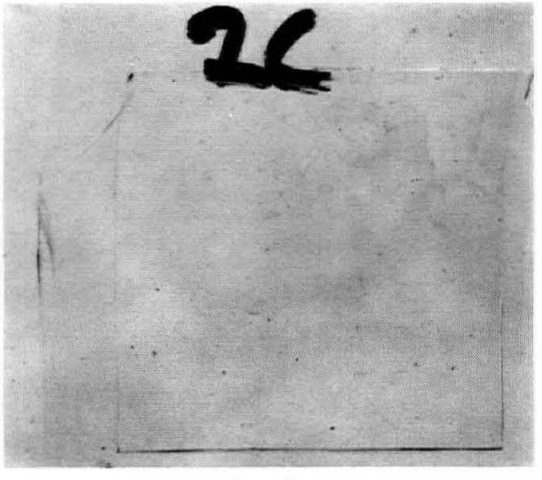
EVA-Sunadex (135°C, Dark)



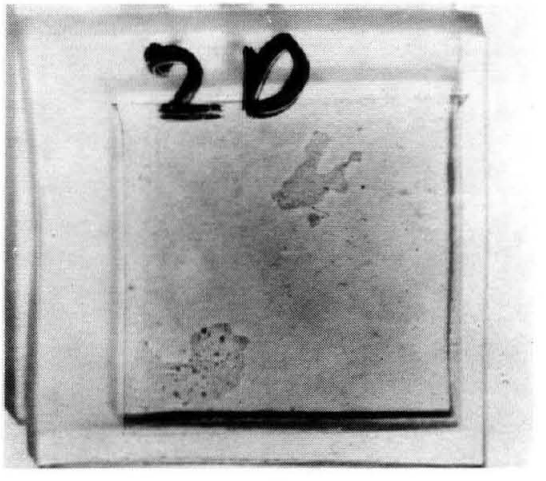
1.0 WEEK



2.0 WEEKS

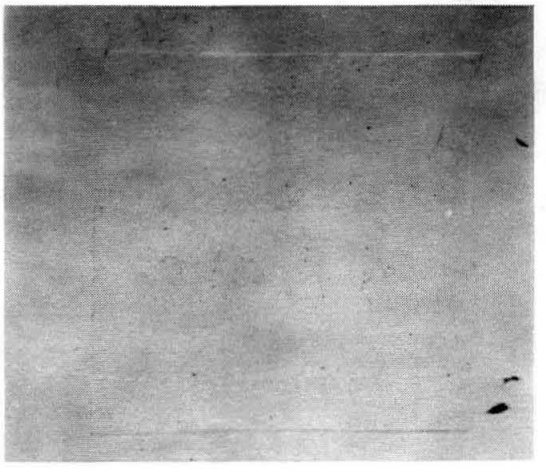


4.0 WEEKS

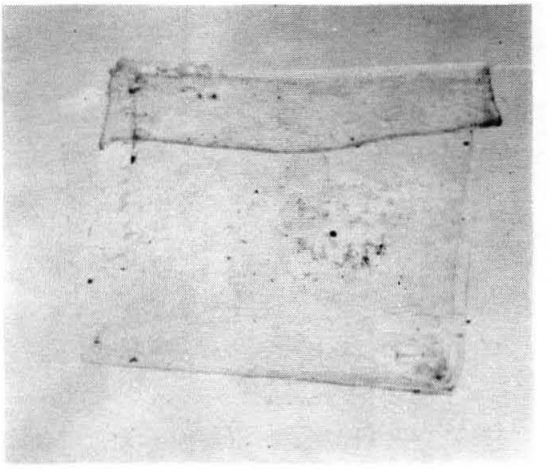


6.0 WEEKS

EVA: No Cover (135°C, 6 suns)



0.5 WEEK



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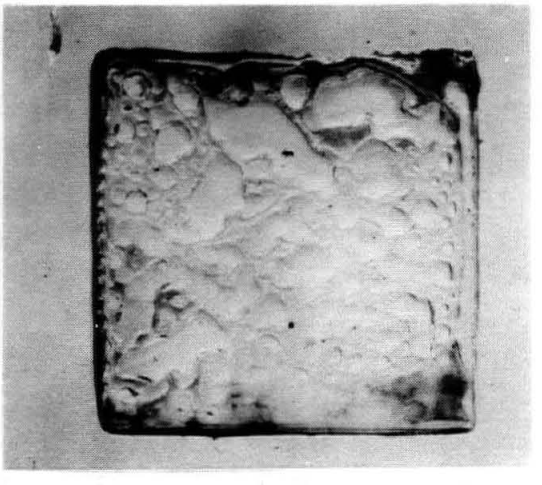

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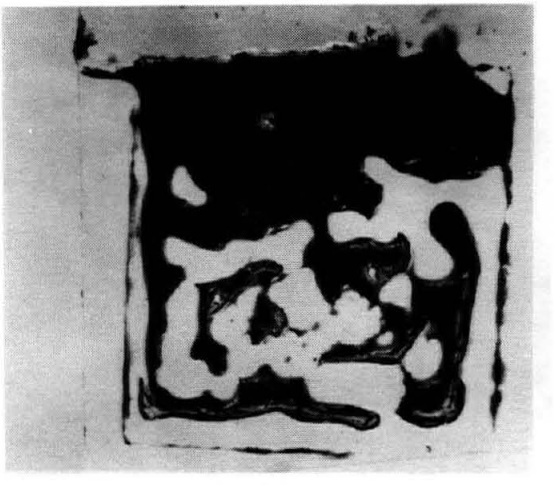
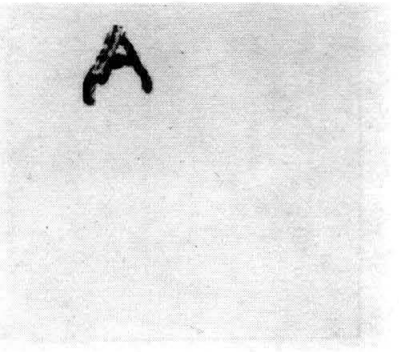


4.0 WEEKS

EVA-Sunadex (135°C, 6 suns)



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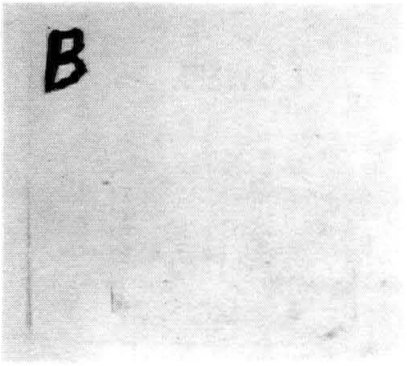
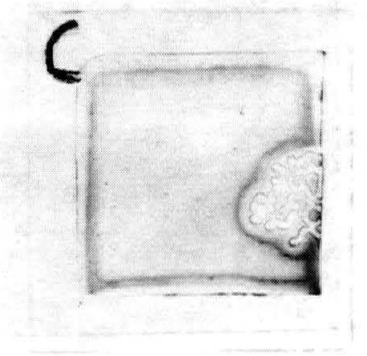


1.0 WEEK



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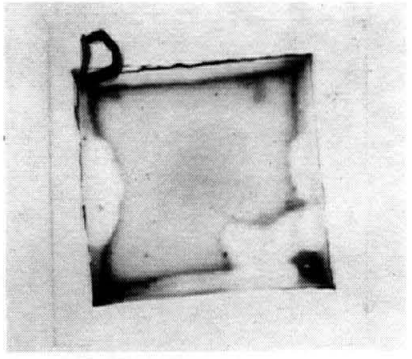
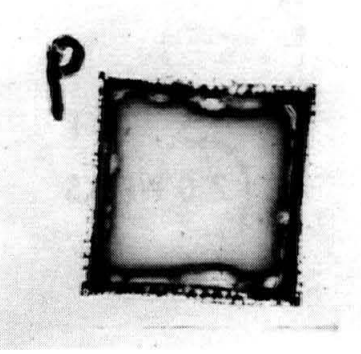
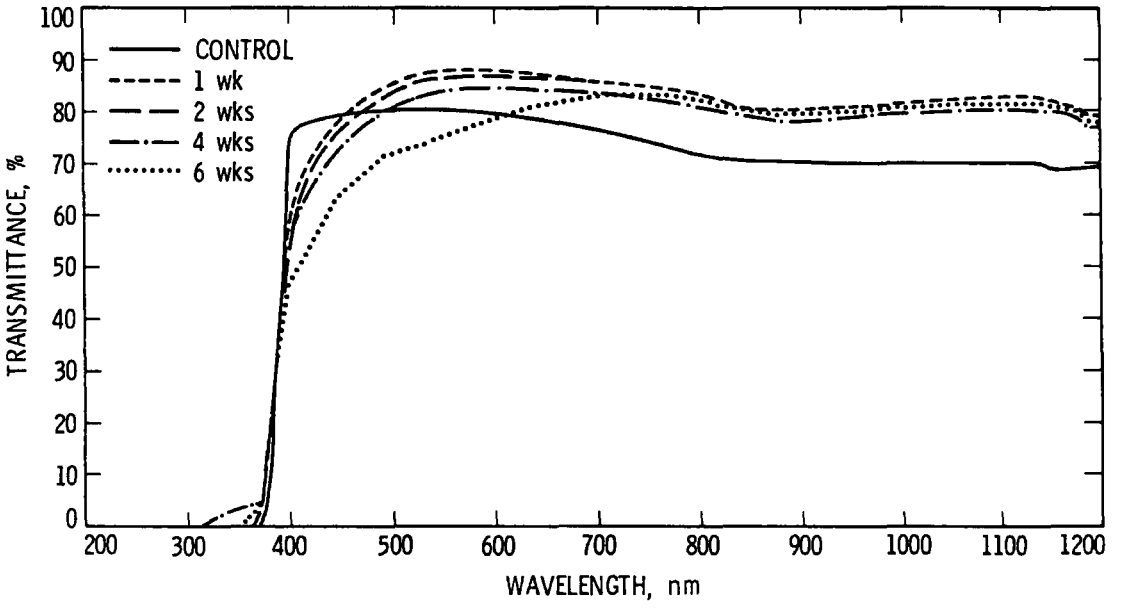


4.0 WEEKS

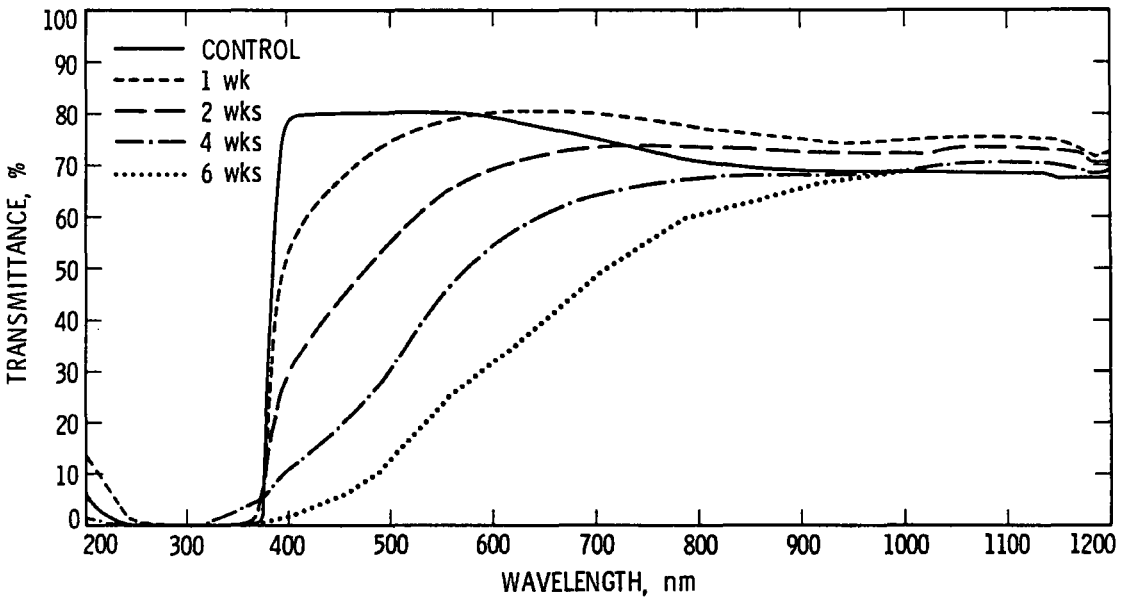


6.0 WEEKS

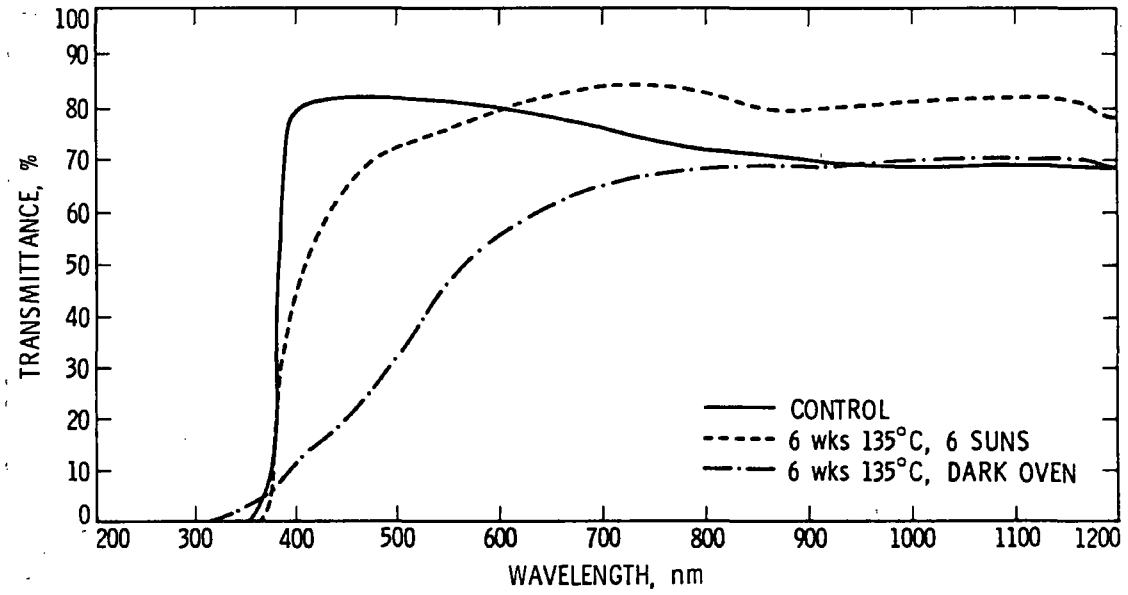
Transmittance Spectra of PVB-Sunadex (135°C, Dark Oven)



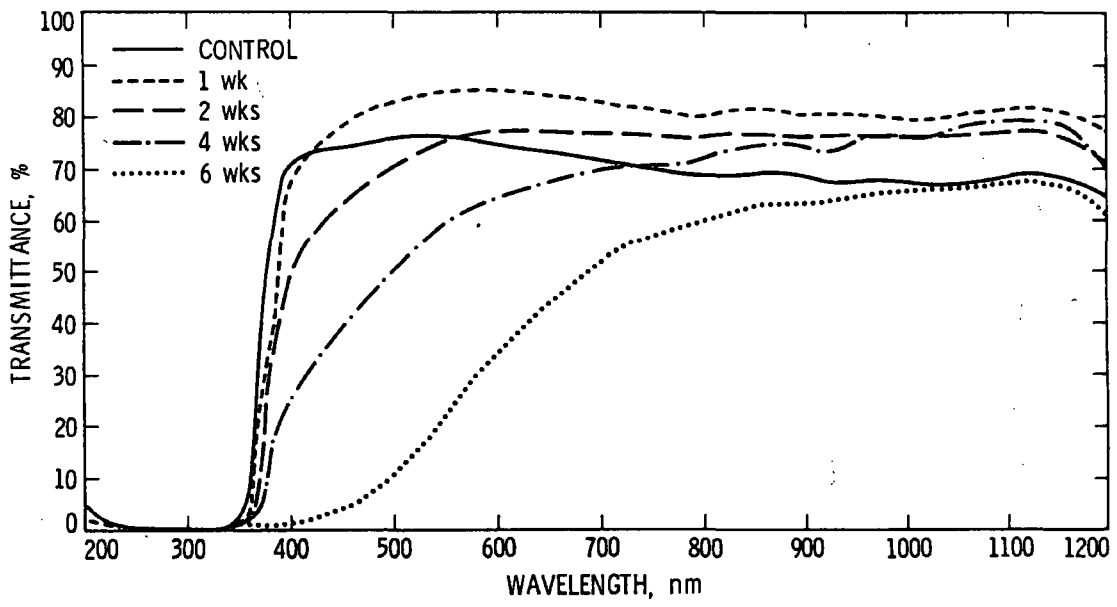
Transmittance Spectra of PVB-Sunadex (135°C, 6 suns)



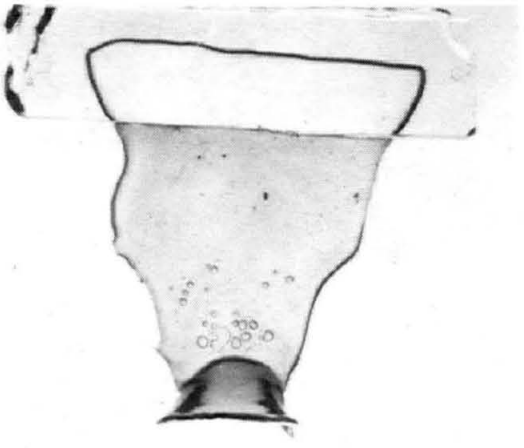
Transmittance Spectra of PVB-Glass



Transmittance Spectra of EMA-Sunadex (135°C, 6 suns)

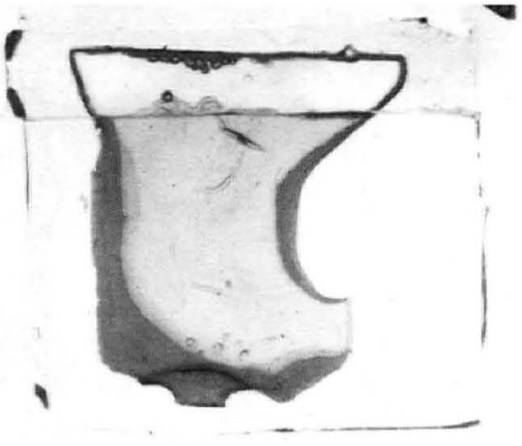


PVB: No Cover (135°C, 6 suns)

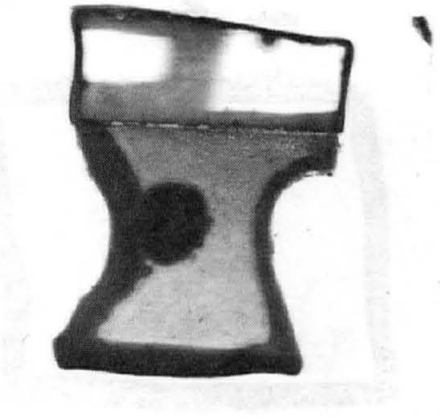


0.5 WEEK

1.0 WEEK



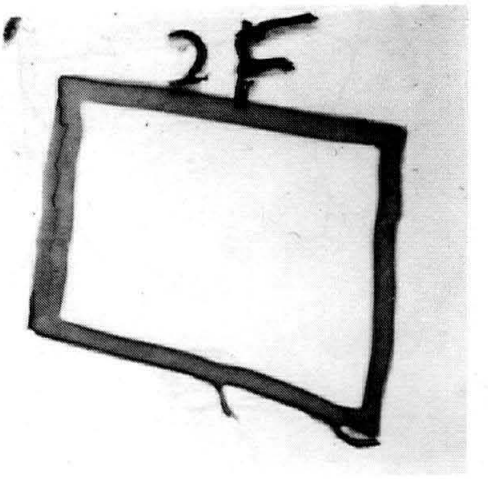
2.0 WEEKS



4.0 WEEKS

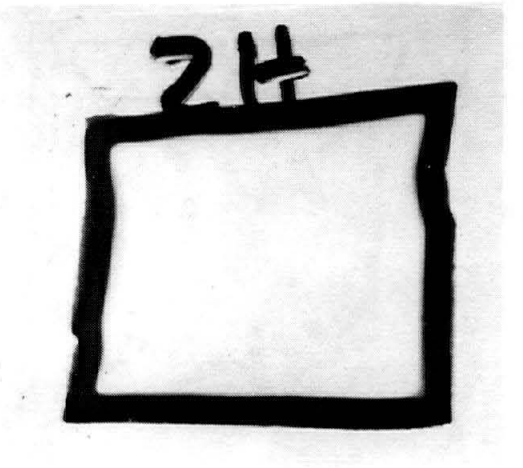
PVB-Sunadex (135°C, Dark)

1.0 WEEK



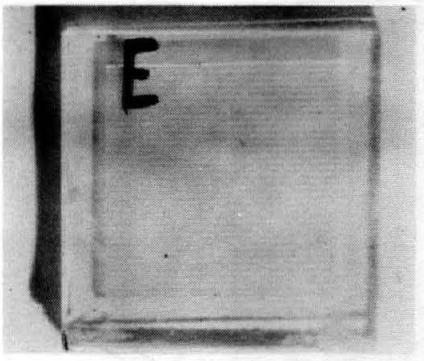
2.0 WEEKS

4.0 WEEKS



6.0 WEEKS

PVB-Sunadex (135°C, 6 suns)



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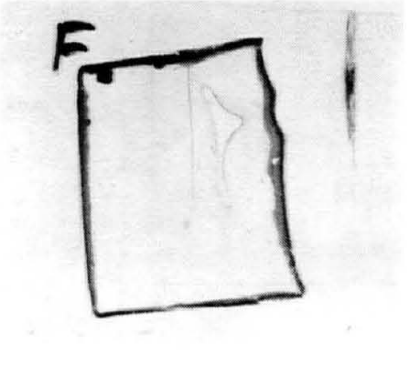
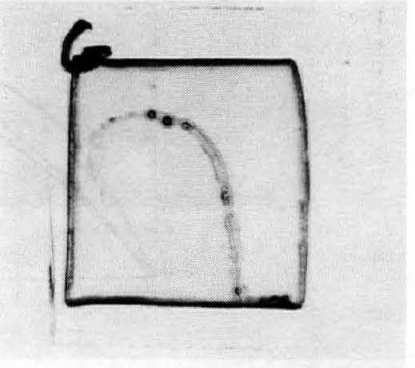


1.0 WEEK



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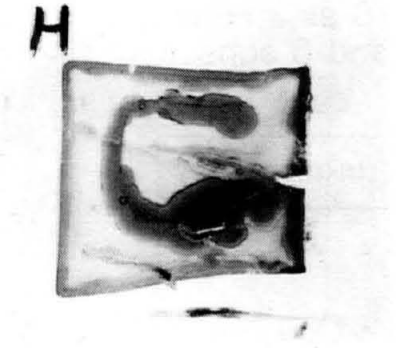
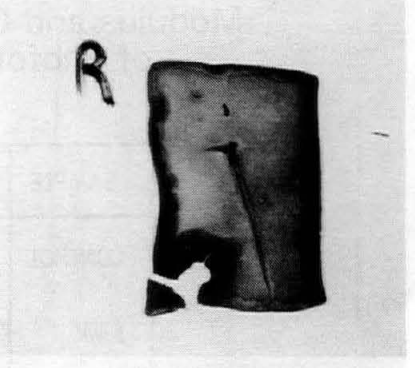
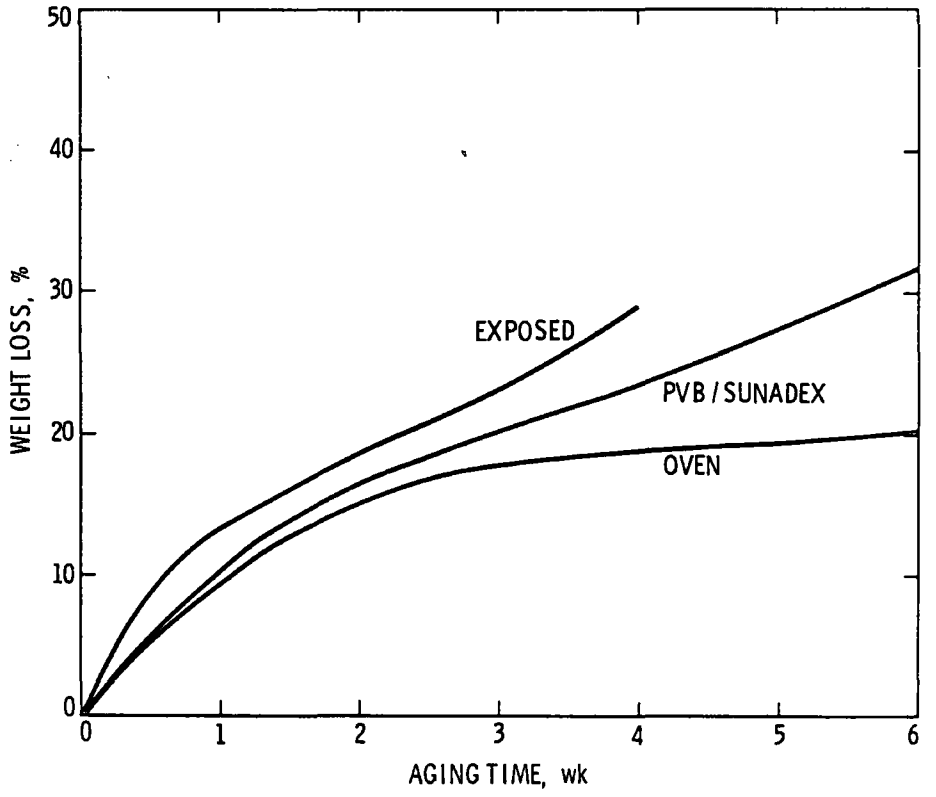


4.0 WEEKS



6.0 WEEKS

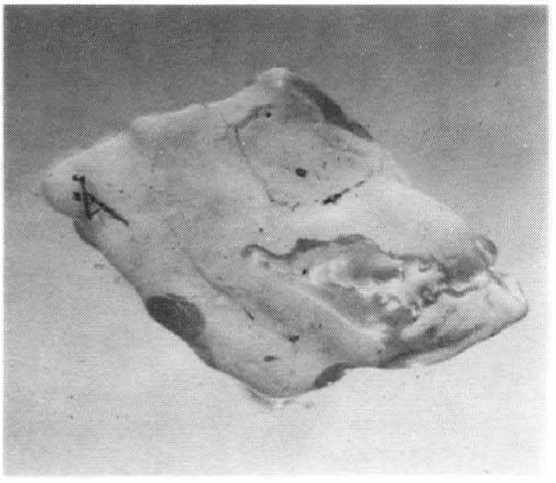
Weight Loss of PVB at 135°C



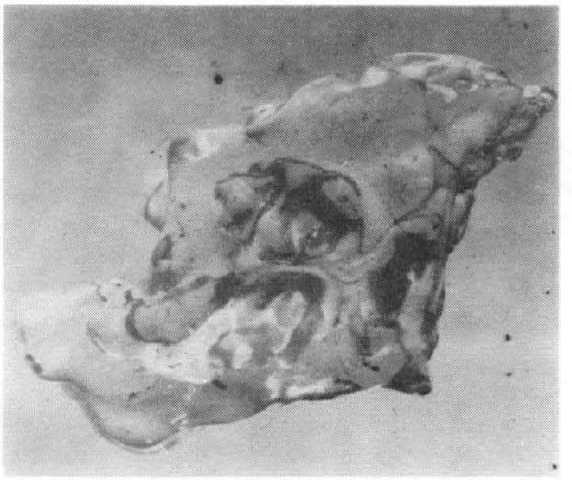
Modulus and Crosslinking Density of PVB as a Function of Photothermal Aging at 135°C and 6 suns

SAMPLE	MODULUS (psi, 5% STRAIN)	CROSSLINKING DENSITY
CONTROL	348	4.8×10^{-4}
1 wk	638	8.9×10^{-4}
2 wks	2610	11.8×10^{-4}
4 wks	3920	16.0×10^{-4}

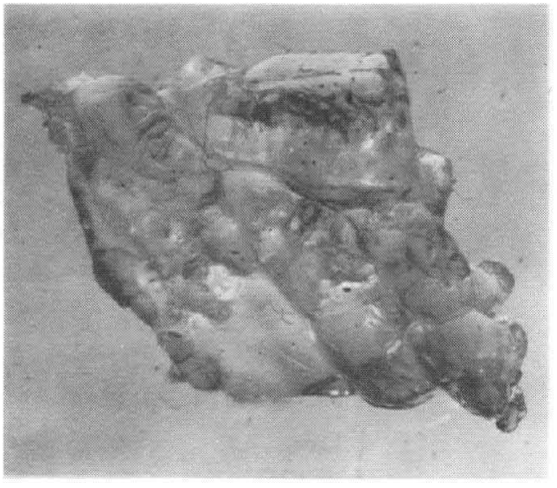
EMA: No Cover (135°C, 6 suns)



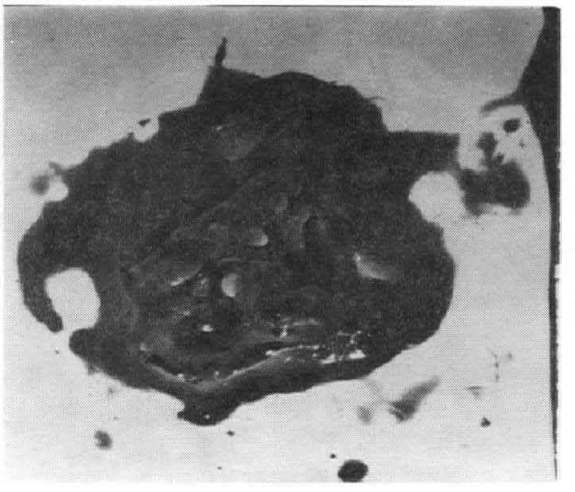
0.5 WEEK



1.0 WEEK



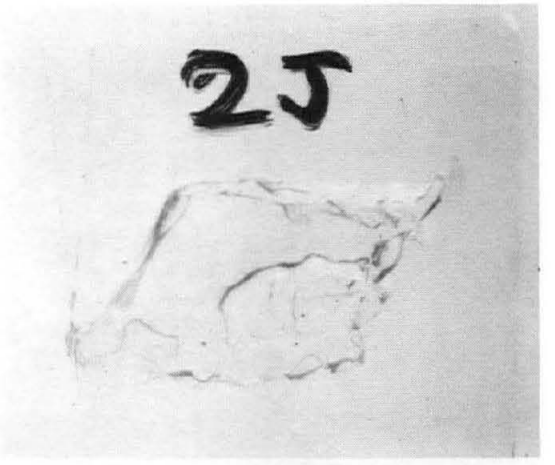
2.0 WEEKS



4.0 WEEKS

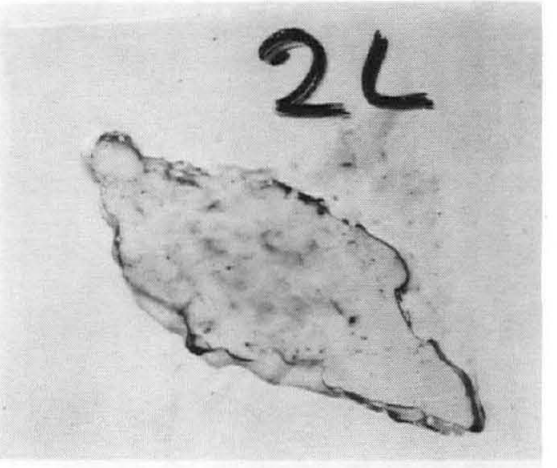
EMA-Sunadex (135°C, Dark)

1.0 WEEK



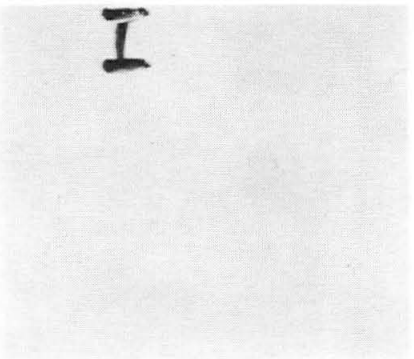
2.0 WEEKS

4.0 WEEKS

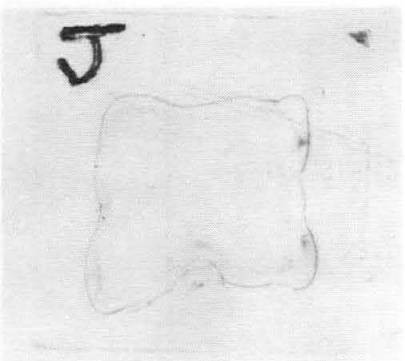


6.0 WEEKS

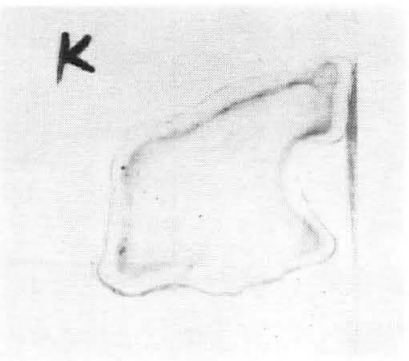
EMA-Sunadex (135°C, 6 suns)



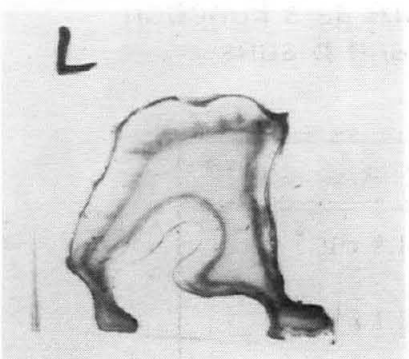
CONTROL



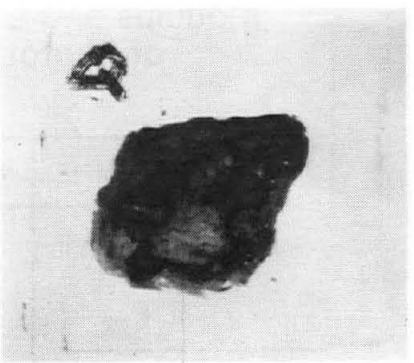
1.0 WEEK



2.0 WEEKS

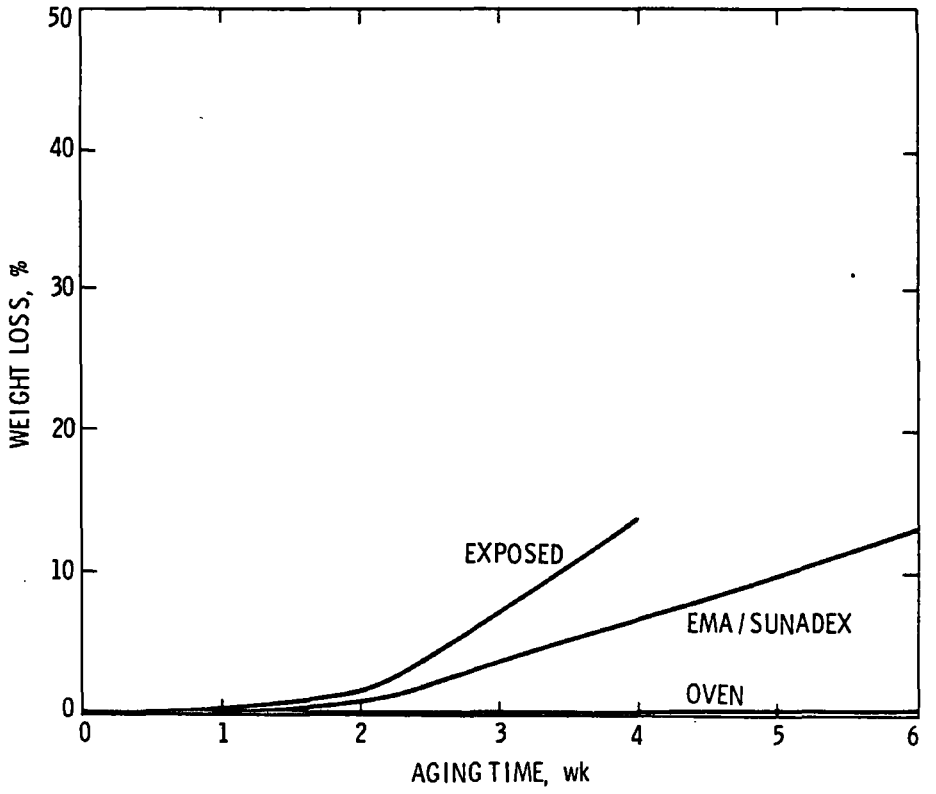


4.0 WEEKS



6.0 WEEKS

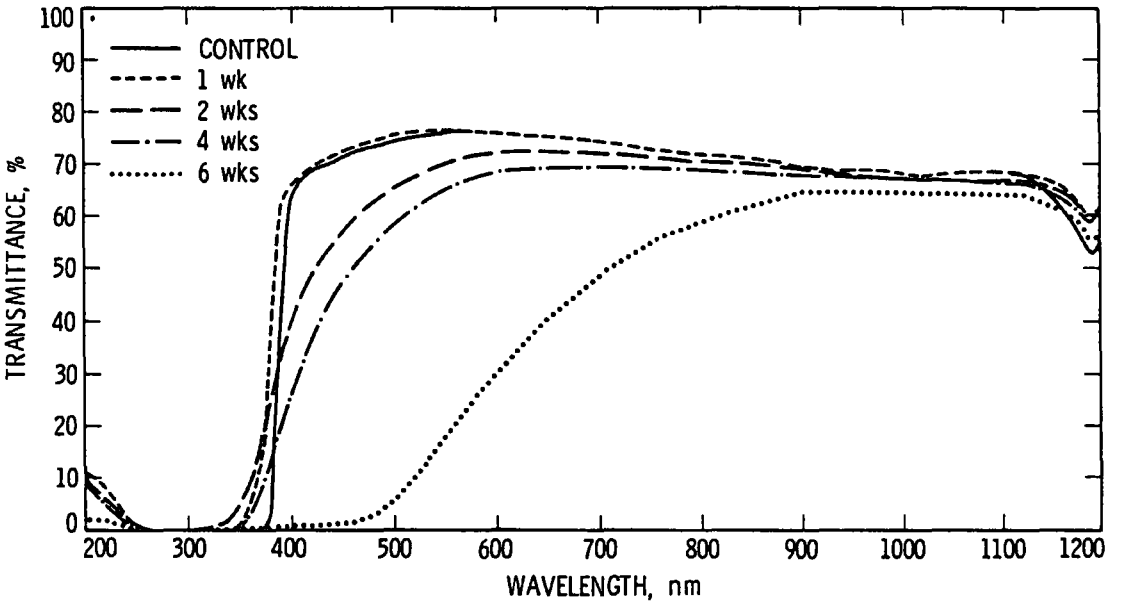
Weight Loss of EMA at 135°C



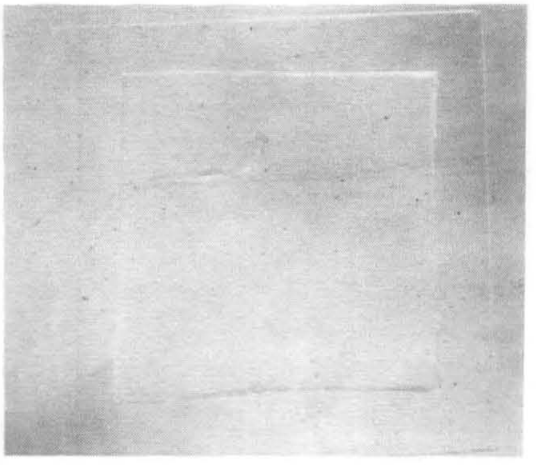
Modulus and Crosslinking Density of EMA as a Function of Photothermal Aging at 135°C and 6 suns

SAMPLE	MODULUS (psi, 5% STRAIN)	CROSSLINKING DENSITY
CONTROL	3567	1.9×10^{-4}
1 wk	3016	1.1×10^{-4}
2 wks	2871	0.8×10^{-4}
4 wks	2552	1.0×10^{-4}

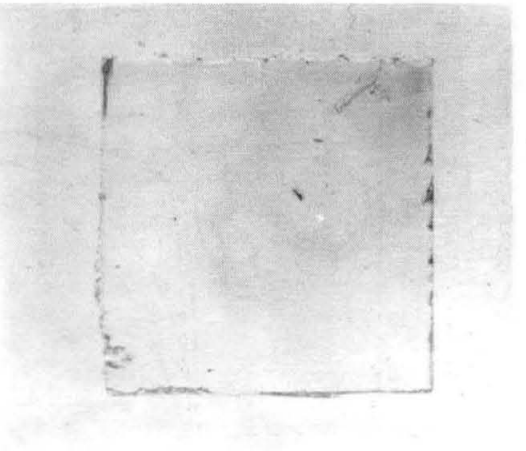
Transmittance Spectra of PnBA-Sunadex (135°C, 6 suns)



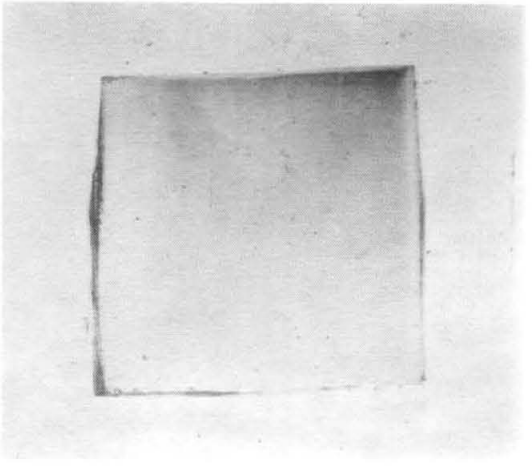
PnBA: No Cover (135°C, 6 suns)



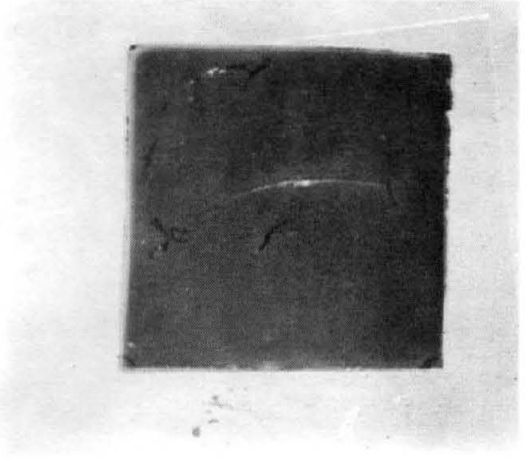
0.5 WEEK



1.0 WEEK

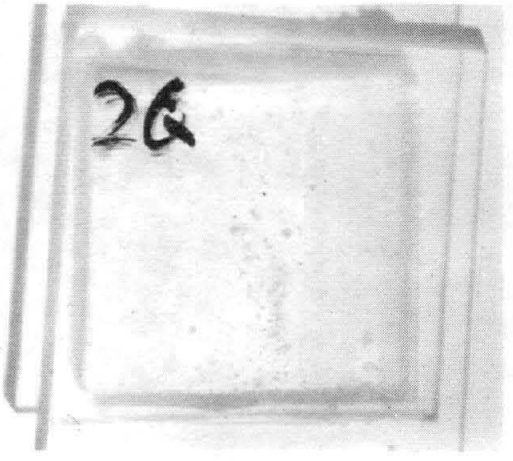


2.0 WEEKS

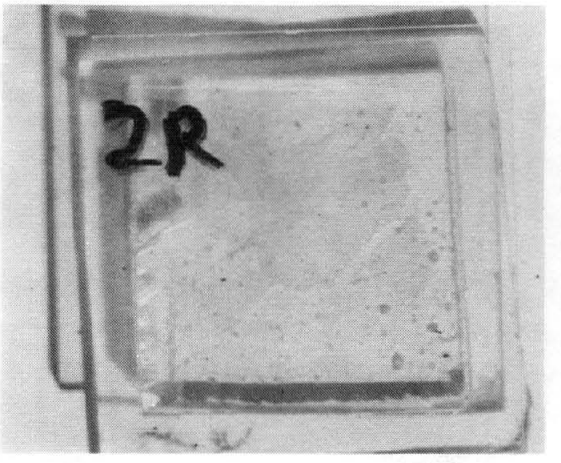


4.0 WEEKS

PnBA-Sunadex (135°C, Dark)



1.0 WEEK



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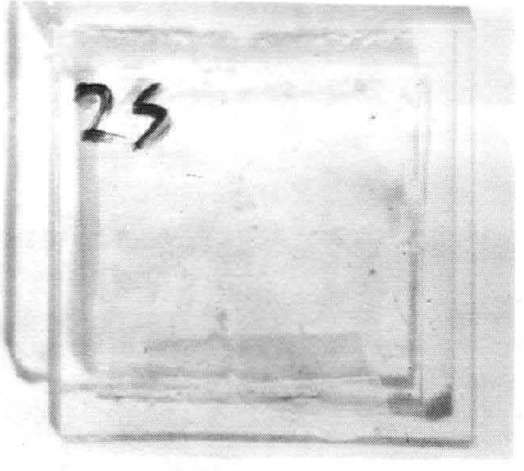
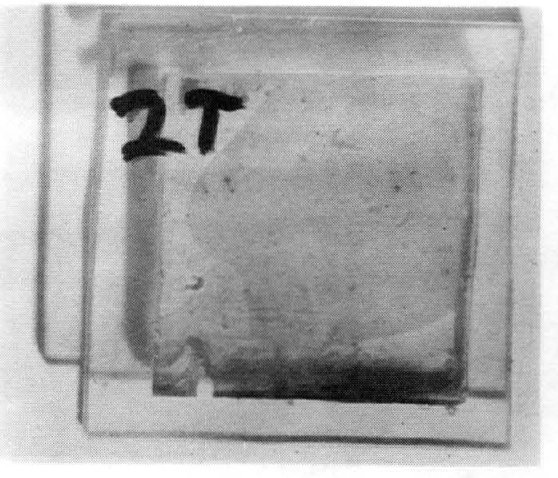
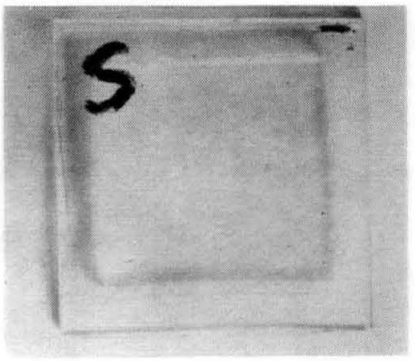


4.0 WEEKS

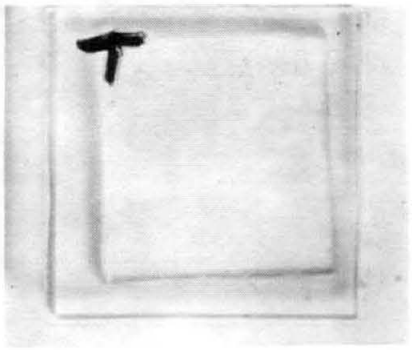


6.0 WEEKS

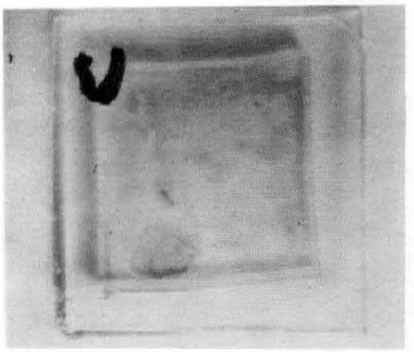
PnBA-Sunadex (135°C, 6 suns)



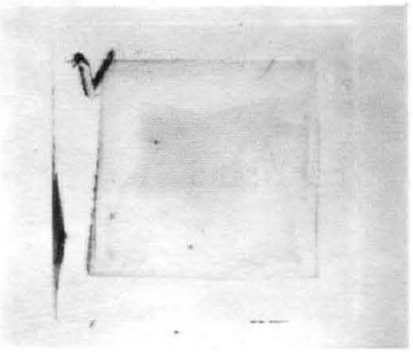
CONTROL



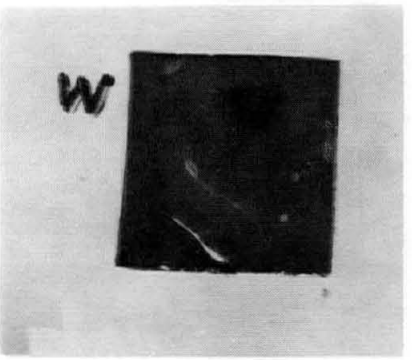
1.0 WEEK



2.0 WEEKS



4.0 WEEKS



6.0 WEEKS

DISCUSSION

QUESTION: Are the temperatures that you report at 6 suns actual sample temperatures or chamber temperatures?

LIANG: These are actual sample temperatures. On every individual sample we have a thermocouple.

QUESTION: Shielded thermocouple?

LIANG: Yes.

OTTH: I was just wondering if you ran any other tests on EVA but 135°C?

LIANG: Yes, we have run a whole series of EVA from 55°C all the way up to 135°C.

OTTH: So you were able to generate, or could if you wanted, a degradation rate for discoloration for EVA then?

LIANG: The discoloration of EVA turned out to be a little bit different. The weight loss seems to be OK. We can extrapolate in terms of temperature. The discoloration, as I mentioned earlier, involves not only the temperature but the photoreaction as well. As long you are involving only the temperature, you can always extrapolate by Arrhenius plot, which is rather straightforward. The problem is, whenever you are involving some chemical reaction, then the acceleration factor in the photon comes into effect and we are still validating that.

WHITE: You mentioned that there were different basic types of cover materials. You mentioned material available from industry and JPL material. I was wondering what the cost relationship was between the JPL material and the industrial materials?

LIANG: I cannot put a price on the JPL development material. The material we developed is basically a copolymer of methyl methacrylate (MMA) with a polymerizable UV stabilizer. The cost of the material is incurred in the synthesis of that polymerizable material. Of course the MMA is relatively low-priced and that will not be a problem.

HUTTEMAN: When you ran your heat experiments with UV-incorporated compounds in the polymers, did you take into consideration or check at all to see if you underwent some morphological change of the UV compound? If you did you would lose your cross-section capturing power of your UV compound and your absorption would go down tremendously and transmission go up.

LIANG: Do you mean have we looked for morphological change?

HUTTEMAN: Have you checked to make sure that the UV compound has not gone from a solution or a dispersion in the polymer to a crystalline compound?

LIANG: We have not checked that. We just looked for transmission characteristics of the material.

HUTTEMAN: You might be undergoing a morphological change. The second question I have is, when you ran the heat experiments and saw yellowing, did you run a control along with them without incorporated UV? Are you sure the UV compound is the one that is degrading and giving you the yellowing?

LIANG: We have run the pure PMMA without UV screener. We did not run a full spectrum of compounds with no UV stabilizer. But we did not detect any changes in pure PMMA.

HUTTEMAN: OK.

LIANG: On the morphological change, we have also monitored the weight loss on these thin films and there seems to be a correspondence in terms of the gradual weight loss on these thin-film materials. So that gave us a very good feeling that we are indeed losing some material.

GUILLET: How did you measure your crosslink density?

LIANG: We did swelling tests.

WILSON: May I see the data on Tedlar UV screening film ? While you are getting that out let me mention the fact that UV screening agent is not a stabilizer. That film, 100BG30UT, was developed to protect substrates under it. I believe you said you found some initial changes, but you didn't see any more changes. I would like to get a copy of that to have some of our people look at it. I have a suspicion of what is happening. Let me ask another question. Did you check to find out? There are two ways that one can conceive, three counting the crystallization, but there is also the possible reaction of some material which is screened, with which the UV initiates a reaction and it disappears, or it changes chemical species. Did you look into that?

LIANG: We did not look into that because we do not know the UV screening stabilizer. Now if you can provide me some of that information I will be happy to do it. There are indeed two reactions associated with this. We actually run Tedlar at various temperatures trying to get an overall activation energy and it turns out to be somewhere between 12 and 13 kilocalories per mol. If you look at that typically physical reaction, you are looking at less than 10 kilocalories per mol. This is right on the borderline, but seems to be a little bit high for physical leaching. It is conceivable that there could be a photochemical reaction taking place which is depleting the material, rather than just physical leaching.

WILSON: I can only say, don't assume that it is exuding and disappearing. That may not be correct. I don't recognize the designation of this Tedlar from the UTB100 and I would like to have our people look at the fingerprints and see what it is like. You also mentioned an acrylic film which you irradiated on one side. To what did you attribute the changes in this surface?

LIANG: Let me answer that question in general. Typically if you are trying to disperse some UV absorber in a polymer and trying to stabilize it by merely providing some sort of screening effect, you will always run into some problem on the surface. Let's say you are putting in 5% stabilizer,

on the surface you still have 95% of the unprotected polymer and only 5% of the stabilizer. So on the back of the film, the polymer has the benefit of the protection of the screening but 95% of the material on the surface will not be protected. That is why surface degradation precedes bulk degradation. The acrylic film that I mentioned to you earlier is a polymethyl methacrylate (PMMA) film, supposedly pure PMMA not degradable in the outdoors. We have shown in our chamber that PMMA does not degrade. The reason why we think this particular acrylic film is degrading is that whenever we try to introduce chemically the UV absorber, we are simultaneously introducing a weak link into the PMMA backbone. Chemically, it is called tertiary hydrogen. What we did was, we developed a vinyl derivative of the UV absorber and we copolymerized onto a PMMA backbone and the problem with the vinyl group is that you are introducing a vinyl tertiary hydrogen which was not previously present in pure PMMA, and we believe this is the weak link in the material and that is more susceptible to an oxygen attack leading to photooxidation.

WILSON: Have you considered morphological changes in the fine structure of the film surface which can happen irrespective of any chemical changes? If not, it might be something to look at.

LIANG: Yes. In fact, morphologically you can do a surface analysis. For instance, one can measure the contact angle, the wettability, as a function of aging time. If the material is getting rougher, for instance, you will see a decrease in the contact angle. We have tried various solvents with different polarity and we have found that indeed the material may be getting rough but that roughness alone cannot explain the extent of changes in contact angle. Therefore, there must be a polarity change on the material surface as well. We are, at the same time, as you'll hear from various speakers, trying to develop photoacoustic techniques which are a lot more sensitive in picking up this photooxidation. We are going to take this film down there and subject it to a photoacoustic test and see if we can pick up the hydroxyl group, therefore more definitively pinpoint the photooxidation.

WILSON: This film here--how long would you say it would protect something under it?

LIANG: If it was only a thermal-activated reaction, it would be a simpler test. You can always use the Arrhenius plot, take the energy activation and extrapolate it. But if it is not, then it would be a completely different story. If you are assuming an activation energy of 12 kilocalories and you extrapolate it to 25°C, you can easily get 7 to 10 year's screening lifetime out of it. You can extrapolate it by Arrhenius relationship.

WILSON: If that is indeed 100DG30UT Tedlar, there are hundreds of installations of materials which are affected by UV screening which have been out from 8 to 12 years in which the film has continued to protect it quite well. That is why I would like to have some of our people look at the fingerprints.

LIANG: Sure. Again, I want to say we are only looking at the relative behavior of materials. Absolute lifetime would have to be determined and that is what we are doing. Absolute lifetime prediction

must be based on particular reaction mechanisms. Again, as I said, if it was only thermal it would be straightforward to do.

KETOLA: Although in the talk this morning it was implied that exposure in the CER was directly translatable to exposures to outside on the same scale; it was implied that there was a linear relationship. Now you are saying it is not.

LIANG: Let me remind everybody here that whenever you try to validate accelerated testing you have to keep in mind it is process- and material-specific. This morning what Ami Gupta showed is a photooxidation specifically applied to EMA. It is a photoreaction, so therefore when we calibrate--let's say we do 6 suns--we know we are accelerating 6 times on the photon flux. We know exactly the reaction mechanism at that point. When you are talking about a reaction which involves both thermal and photons, now that is a completely different story. You have to be specific in that. Again, like I said, if it is a simple thermal reaction, it is easy, you use an Arrhenius plot and you extrapolate it out. When you involve photons together with thermal, now that is a completely different thing. That is the reason why I said it is not exactly the same.

QUESTION: Is the exposure of the EMA film only at 6 suns and at room temperature, or was that an elevated temperature?

LIANG: No. EMA was done at 35°C and 20 suns (in the 295 nm -370 nm wavelength region). The outdoor exposure was also at 35°C, 1 sun. So you see a correlation between the photons while the temperature remained constant.

WILSON: What were the conditions in the CER on that particular slide?

LIANG: This was carried out at 6 suns, 85°C, and was also subject to rain and water extraction--

WILSON: 85°C.

LIANG: And also subject to water extraction as well. So there is water sprayed on. For every 22 hours of irradiation there is also 2 hours of water spraying.

KRISHNAN: There are several small molecules like the UV absorber that one could extract out with an organic solvent. If the difference in these two spectra are just a morphological or crystallization effect, you can extract your samples, and if you get the same amount of UV absorber from both of them it is indeed a crystallization effect.

LIANG: I see. We have actually tried to do that. If you remember earlier I said that the FTIR data indicated that we can account for those losses on the FTIR spectrum by the amount of the extractable or the loss that we can take out.