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**Modelling of Polymer Photodegradation
for Solar Cell Modules**

**A Quarterly Technical Progress Report
Covering the period January 1 - March 31, 1981**

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**(NASA-CR-165041) MODELLING OF POLYMER
PHOTODEGRADATION FOR SOLAR CELL MODULES
Quarterly Technical Progress Report, 1 Jan.
- 31 Mar. 1981 (Toronto Univ.) 17 p
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08482**

CSCS 07C G3/27

LSA Project, Technology Development Area

Contract Goals and Objectives

As part of the Encapsulation Task, this research program is intended to model the photodegradation of synthetic polymers used as pottants and/or cover sheets in the LSA solar cell module designs. It involves the development of a computer simulation of the chemical processes that take place under weathering conditions which could, in principle, relate directly to the performance of these materials and afford some basis for predicting and/or controlling their useful lifetimes.

The program can be divided into three main parts:

1. The development of a computer program to model the weathering/ photooxidation of an ethylene-vinyl acetate copolymer as a typical candidate for LSA applications.
2. The development of new analytical procedures for the determination of photooxidation and photodegradation at early stages in solid polymer samples.
3. The development of weathering tests suitable for use with a computer kinetic model to provide a basis for extrapolated predictions.

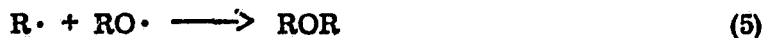
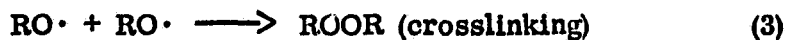
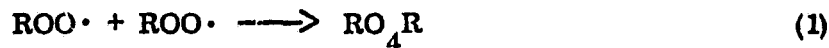
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Summary

1. Computer Simulation of Photooxidation

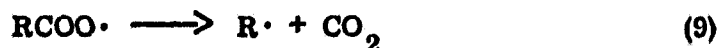
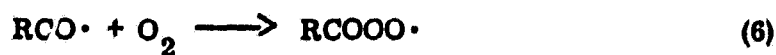
In the first year of the contract, a computer model which includes an integration routine originally advanced by Gear* was developed and demonstrated to simulate, in principle, the chemical changes which may occur in the photooxidation of hydrocarbons, using as input data a set of elementary reactions, corresponding rate constants and appropriate starting conditions. Application of this model to the photooxidation of pollutant and plastic materials used in the LSA module designs should provide for the first time a reliable predictive capability regarding the useful lifetime of these materials.

During the first quarter of this year the general mechanism of elementary reactions has been reviewed and improved. The earlier mechanism consisting of 46 reactions has been simplified considerably by reducing the number of formal termination steps since it became apparent that the major termination process goes via the peroxy radicals. Thus, we have eliminated all the other radical terminations and disproportionations, retaining only the following:



In addition, we have included new reactions of oxygen with acyl radicals (from Norrish type I) to form peracids, which then decompose to form carbon dioxide:

* C. W. Gear, Comm. ACM, 14, 176 (1971).



We have also eliminated the sensitized decomposition of BOOH by energy transfer from excited ketones, and reduced the value of the rate constant for the sensitized decomposition of ROOH ($k = 10^8$). The photochemical reactions of small ketones formed by the Norrish type II process have also been added for completeness. The result is that we now have to deal with 36 reactions (down from 46) and 30 different species (down from 33).

Having changed the mechanism significantly, the integration parameters require manipulation to afford appropriate results on a realistic time-scale. We are now in the process of gaining hands-on experience of varying the integration parameters by feeding different input data to the computer. No dramatic differences have been observed to modify any of our earlier conclusions, namely that the major products predicted are ketones, alcohols and water with both scission by ketone cleavage and some crosslinking by radical recombination taking place (see Appendix).

The computer output shows the predicted concentration profiles of all the chemical species involved over time but the short time scale of days and hours implies more work on our model is necessary.

2. Photooxidation of Model Alkanes

We have continued to monitor the photooxidation of n-decane and 2,4-dimethyl pentane (DMP) initiated with peroxide and/or ketone as models for the photooxidation of polyethylene and ethylene segments of EVA in order to validate the general mechanism and computer product simulation.

The major products have been established earlier to be isomeric ketones, alcohols and water. To get clearer insight into the mechanism we have been

doing finger-print analysis on the GC to identify the other products of photo-oxidation. This has proven to be an elusive exercise to date, but our efforts are continuing. We have also made preparation for LC analysis to attempt more effective and reproducible product separation. Some unavailable expected products are currently being synthesized for use as standards.

3. EVA Automated Viscometry

We have irradiated solutions of ELVAX in methylene chloride and measured the viscosity for different amounts of irradiation time in automated sequence. The neat ELVAX in solution shows a linear increase in viscosity with time of irradiation. This implies that the EVA crosslinks to some degree on irradiation (Figure 1).

Samples of additives used in the formulation to stabilize EVA have been supplied from Springborn Laboratories. We have also measured the viscosity changes in solutions of ELVAX containing up to 10% NAUGARD P (Uniroyal) or Cyasorb UV 531 (a substituted benzophenone from American Cyanamid). There is a similar linear increase in viscosity of these solutions showing the absence of any stabilization effect in solution.

The observation of increased viscosity, which strongly suggests that crosslinking is a major process, implies that there is a more likely possibility of the practical degradation of these materials deteriorating by shrinking and stripping from supports as the crosslinking takes place rather than the alternative embrittlement normally due to polymer scission and lower molecular weight.

We would now like to irradiate films of ELVAX with and without the additives and then measure the viscosities of the solutions formed by dissolving the irradiated films to measure the effectiveness of these stabilizers on EVA in the solid state.

Exposure of both clear and white EVA film samples to outdoor weathering conditions is being continued at EcoPlastics Limited. Some weatherometer experiments are also being planned.

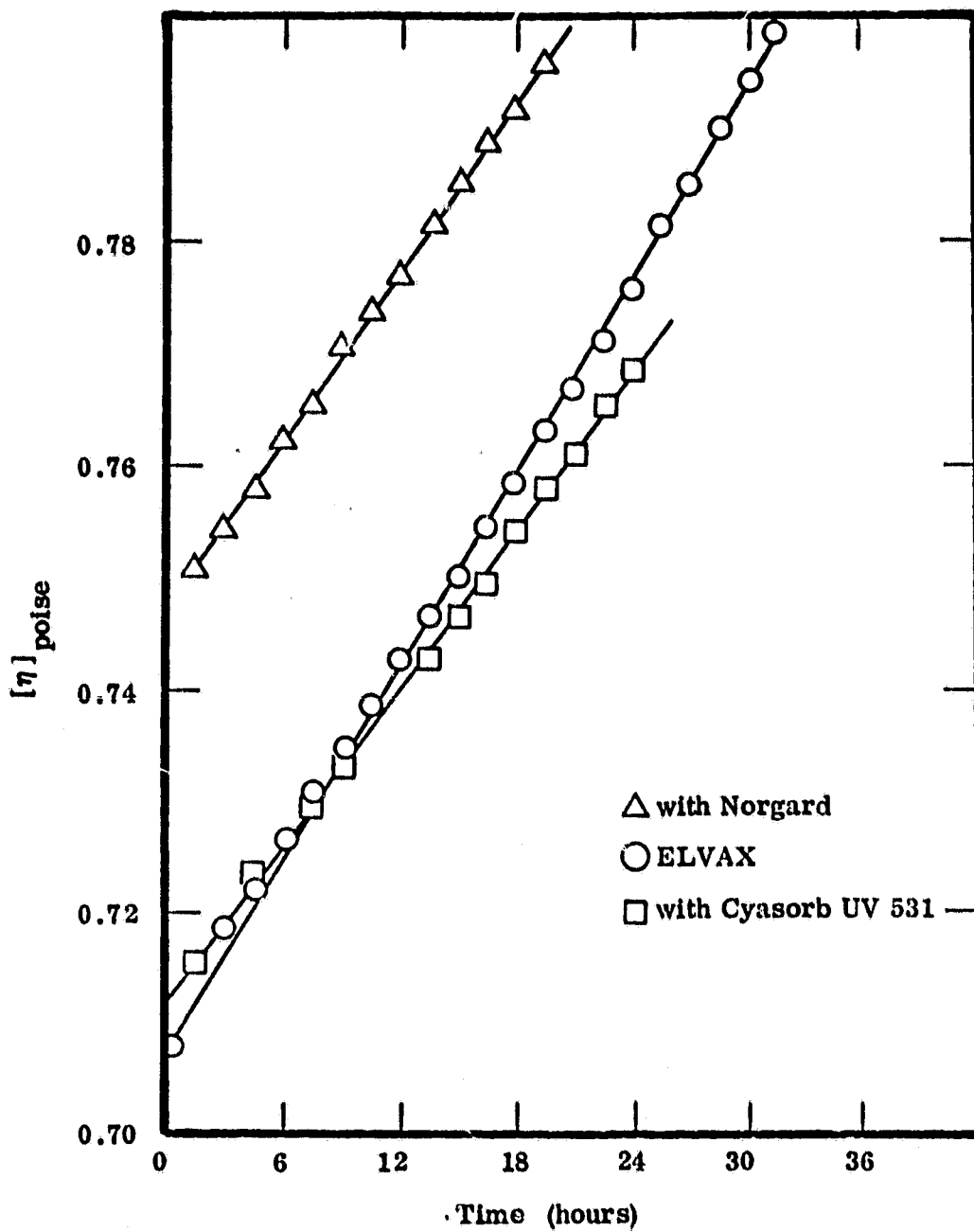


FIGURE 1. Intrinsic viscosity vs. irradiation time (ELVAX 0.47 g/100 ml CH_2Cl_2)

Appendix

Some Examples of Input-Output Data Used in the Current

Simulation Routine for Alkane Photooxidation

1	I2	UH	+ RH	-> R	+ HOH	
2	P2	ROO	+ RH	-> R	+ ROOH	
3	P1	R	+ O2	-> ROO		
4	P4	R	+ ROOH	-> ROO	+ RH	
5	P5		ROOH	-> RO	+ OH	
6	P6	RO	+ RH	-> ROH	+ R	
7	P7	ROO	+ ROO	-> RO4R		
8	P8	CROO	+ CROO	-> CRO	+ CRO	+ SO2
9	P9		RO4R	-> CROO	+ CROO	
10	P10	CROO	+ CROO	-> ROH	+ KETONE	+ SO2
11	P11		CRO	-> RO		
12	P12	ROO	+ ROO	-> ROH	+ KETONE	+ SO2
13	P13		RO	-> R	+ KETONE	
14	P14		KETONE	-> KET		
15	P141		SMKETONE	-> KET		
16	P15		KET	-> SM/R	+ RCO	
17	P151	SMR	+ RH	-> SMRH	+ R	
18	P152	RCO	+ RH	-> ALDEHYDE	+ R	
19	P153		RCO	-> SMR	+ CO	
20	P154	RCO	+ O2	-> RCOOO		
21	P155	RCOOO	+ RH	-> PERACID	+ R	
22	P156		PERACID	-> RCOO	+ OH	
23	P157		RCOO	-> R	+ CO2	
24	P16		KET	-> ALKENE	+ SMKETONE	
25	P161	KET	+ O2	-> KETONE	+ SO2	
26	P162		KET	-> KETONE		
27	P163		SO2	-> O2		
28	P18	KET	+ ROCH	-> KETONE	+ RO	+ OH
29	P19	CRO	+ CRO	-> ROOR		
30	P20		CROO	-> ROO		
31	P21	SO2	+ ALKENE	-> ROOH		
32	P22	R	+ ALKENE	-> BRANCH		
33	T3	RO	+ OH	-> ROOH		
34	T6	RO	+ RC	-> ROOR		
35	T7	R	+ R	-> RR		
36	T10	R	+ OR	-> ROR		

INITIAL CONCENTRATION DATA (MOLES/L)

*****VARIABLE SPECIES*****CONCENTRATION*****

*				*
*				*
*	1	OH	0.0	*
*	2	RH	0.50000D+01	*
*	3	R	0.10000D-03	*
*	4	HOH	0.0	*
*	5	ROO	0.0	*
*	6	ROOH	0.0	*
*	7	ROR	0.0	*
*	8	RO	0.0	*
*	9	ROH	0.0	*
*	10	RO4R	0.0	*
*	11	CROO	0.0	*
*	12	CRO	0.0	*
*	13	SO2	0.0	*
*	14	KETONE	0.0	*
*	15	KET	0.0	*
*	16	SMKETONE	0.0	*
*	17	SMR	0.0	*
*	18	RCO	0.0	*
*	19	SMRH	0.0	*
*	20	ALDEHYDE	0.0	*
*	21	CO	0.0	*
*	22	RCOO	0.0	*
*	23	PERACTO	0.0	*
*	24	RCOO	0.0	*
*	25	CO2	0.0	*
*	26	ALKENE	0.0	*
*	27	RUDR	0.0	*
*	28	BRANCH	0.0	*
*	29	RR	0.0	*
*	30	OR	0.0	*

*****CONSTANT SPECIES*****CONCENTRATION*****

*				*
*				*
*	31	O2	0.10000D-02	*
*				*

REACTION RATE CONSTANTS...TEMP=300.0 K...

RXN LABEL	RATE CONSTANT	PRE-EXP FACTOR	E-ACT
1 T2	0.30000D+09		
2 P2	0.10000D+03		
3 P1	0.40000D+10		
4 P4	0.10000D+06		
5 P5	0.30000D-06		
6 P6	0.20000D+06		
7 P7	0.10000D+08		
8 P8	0.25000D+06		
9 P9	0.50000D+10		
10 P10	0.10000D+09		
11 P11	0.10000D+10		
12 P12	0.15000D+07		
13 P13	0.10000D+06		
14 P14	0.30000D-05		
15 P141	0.30000D-05		
16 P15	0.50000D+07		
17 P151	0.10000D+06		
18 P152	0.10000D+06		
19 P153	0.10000D+06		
20 P154	0.40000D+10		
21 P155	0.10000D+04		
22 P156	0.30000D-03		
23 P157	0.10000D+09		
24 P16	0.50000D+08		
25 P161	0.10000D+10		
26 P162	0.10000D+10		
27 P163	0.60000D+05		
28 P18	0.10000D+08		
29 P19	0.10000D+15		
30 P20	0.10000D+10		
31 P21	0.10000D+04		
32 P22	0.10000D+03		
33 T3	0.10000D+10		
34 T6	0.10000D+09		
35 T7	0.30000D+06		
36 T10	0.30000D+09		

***INTEGRATION REQUESTED--STARTING INTEGRATION PARAMETERS FOLLOW**

ITEM	VALUE
INTEGRATION TIME LIMITS--STARTING TIME	0.0 SEC

-->STARTING TIME

TOTAL TIME= 0.0 SEC

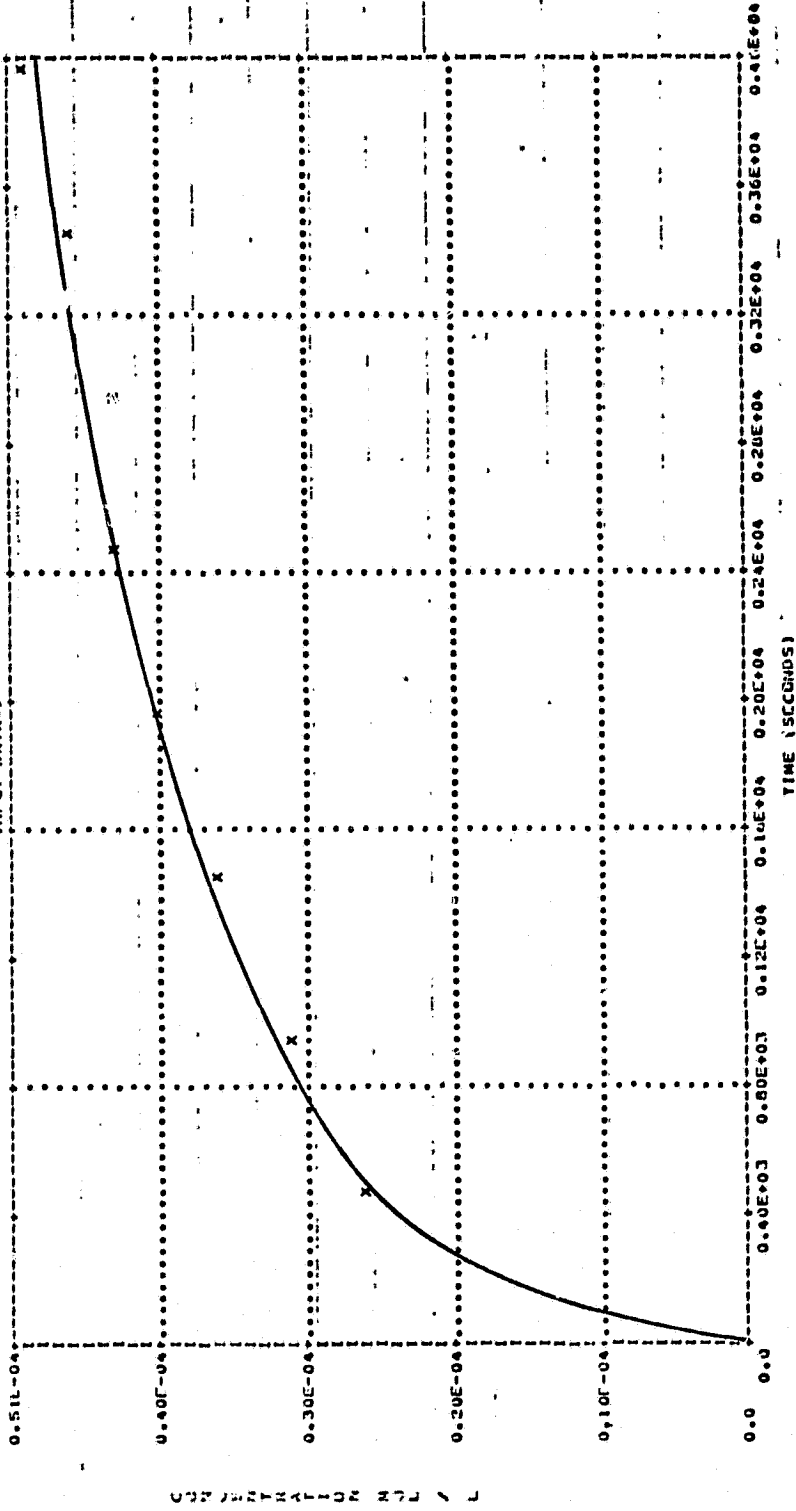
-->STOPPING TIME

TOTAL TIME= 0.30202769D+02 SEC

SPECIES INDEX	SPECIES LABEL	INITIAL CONC (M/L)	FINAL CONC (M/L)
1	OH	0.0	0.31570659D-10
2	RH	0.50000000D+01	0.491220D+01
3	R	0.10000000D-03	0.23680061D-11
4	HOH	0.0	0.12427349D-07
5	ROO	0.0	0.18948880D-07
6	ROOH	0.0	0.15785087D-02
7	ROR	0.0	0.0
8	RO	0.0	0.43049157D-15
9	ROH	0.0	0.50013905D-04
10	RO4R	0.0	0.59843333D-18
11	CROO	0.0	0.71812011D-17
12	CRO	0.0	0.25734825D-37
13	SO2	0.0	0.89788710D-14
14	KETONE	0.0	0.50003502D-04
15	KET	0.0	0.14205389D-18
16	SMKETONE	0.0	0.21429714D-09
17	SMR	0.0	0.14518795D-17
18	RCO	0.0	0.15441170D-18
19	SMRH	0.0	0.21896581D-10
20	ALDEHYDE	0.0	0.23288524D-11
21	CO	0.0	0.46589834D-12
22	RCOO	0.0	0.12356836D-15
23	PERACID	0.0	0.18551706D-10
24	RCOO	0.0	0.05655109D-22
25	CO2	0.0	0.04104169D-13
26	ALKENE	0.0	0.21430684D-09
27	ROOR	0.0	0.43004727D-21
28	BRANCH	0.0	0.11030173D-17
29	RR	0.0	0.37520004D-09
30	OR	0.0	0.0

FIG. 4. SPECIES ROOH

SPECIES LABEL DATA ⇒ ROOH
SYMBOL INPUT DATA ⇒ X



L / L IN MOUNTAIN RANGE

TIME (SECONDS)

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OF POOR QUALITY.

