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DOCUMENTATION PAGE

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1a. REPO **AD-A222 848**	1b. RESTRICTIVE MARKINGS
2a. SECU	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE JUN 15 1990	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 23926.2-MS
6a. NAME OF PERFORMING ORGANIZATION: Case Western Reserve University 6b. OFFICE SYMBOL (If applicable): Physics	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office
6c. ADDRESS (City, State, and ZIP Code) Cleveland, Ohio 44118	7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: U. S. Army Research Office 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAL03-86-K-0166
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Molecular Dynamics of Physical Aging Processes in Polymer Glasses (Experiment and Theory)

12. PERSONAL AUTHOR(S)
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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 9/1/86 TO 1/31/90	16 April 1990	3

16. SUPPLEMENTARY NOTATION
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES FIELD	GROUP	SUB-GROUP	18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
			Polymer Glasses, Physical Aging, Free Volume, ESR, Electron Spin Resonance, Fluorescence Spectroscopy, Positronium, PAS, Positron Lifetime, Annihilation

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

We have studied free volume and aging in PVAc, PMMA, PEMA, and polycarbonates by fluorescence spectroscopy, electron spin resonance (ESR), and positron annihilation spectroscopy (PAS). The product of the ortho-positronium (o-Ps) lifetime τ_3 and its formation probability I_3 has a temperature dependence above T_g that follows that of the total free volume. The product $I_3\tau_3$ shows a significant decrease as a function of time at temperatures below T_g. Some specimens with the same composition and the same free volume yielded different values for the individual factors I_3 and τ_3. This indicates that PAS can distinguish between samples that are indistinguishable by conventional methods. We also obtained preliminary results on simultaneous measurement of the positron lifetime and the momentum of the annihilated positron-electron pair. There is a clear difference between high-momentum and low-momentum lifetime distributions, with a much larger value of I_3 for the high momentum curve. This is what one expects from the higher momentum involved in o-Ps annihilation.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

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STATEMENT OF THE PROBLEM STUDIED

Physical aging is an important factor in determining polymer properties, yet it is difficult to monitor. Conventional methods of measuring the free volume provide a single parameter which is insufficient to predict future behavior, because the evolution of the polymer depends on the distribution of free-volume elements as well as the total free volume. Current methods cannot distinguish between two samples if the samples have the same composition and the same total free volumes, yet these samples may evolve differently because they may have different histories and consequently have different distributions of free-volume elements.

The positron has been shown to be sensitive to changes that occur during physical aging. Therefore we began this study to determine whether positrons could provide polymer aging information that is unavailable from other measurement techniques. The positron provides two parameters that are relevant to polymer aging: 1. The fraction (usually denoted as I_3 in the literature) of incident positrons that form ortho-positronium (o-Ps) atoms in a sample. 2. The mean lifetime τ_3 of these o-Ps atoms. It has been shown that the mean lifetime is sensitive to the free-volume hole size, whereas the o-Ps formation fraction depends on the number of holes.

If two samples of an identical polymer have the same free volume at the same temperature, it is possible that they will age differently because they have different histories. Until now there was no way to predict the aging behavior without knowing these histories. But such samples may be distinguishable in a positron lifetime experiment, if the size distribution of free volume elements in one sample differs from that in the other sample.

The purpose of this study has been to explore the possibility of making such distinctions in a variety of polymers, by comparing the results of positron studies with those of conventional free-volume measurements, thereby developing a calibration for the positron technique, and then devising thermal treatments that produce pairs of samples which have the same free volume at the same temperature but have different thermal histories.

SUMMARY OF IMPORTANT RESULTS

We have studied several polymers (PVAc, PMMA, PEMA, polycarbonates) by means of fluorescence spectroscopy, electron spin resonance (ESR), and positron annihilation spectroscopy (PAS) involving measurements of the lifetime distributions of positrons in the same polymers that were studied by the other methods. Major results are as follows:

1. Comparison of our results with free-volume results obtained by other laboratories, in which dilatometry was employed, shows that the product $I_3\tau_3$ has a temperature dependence above T_g that closely follows that of the total free volume. This result has also been reported elsewhere. The decrease in $I_3\tau_3$ primarily results from a decrease in τ_3 rather than I_3.

2. Using a sample chamber with high thermal stability at temperatures between -190 C and +150 C, combined with a new extremely efficient high-resolution positron lifetime apparatus, we have studied the behavior of the product $I_3\tau_3$ as a function of time at temperatures below T_g, and have found a decrease as the sample ages (over a period of days) and the free volume decreases. We have also found that this decrease (whose magnitude is about ten times the uncertainty in the individual values of $I_3\tau_3$) primarily results from a decrease in I_3 rather than τ_3, in contrast to the decreases observed as temperature is reduced above T_g. This feature of our results was subsequently reported by others from work on other polymers.

3. Interpreting our aging results on the provisional assumption that the product $I_3\tau_3$ is proportional to the free volume, we found cases in which specimens with the same composition and the same free volume yielded different positron lifetime distributions; i.e., they had different values for the individual factors $I_3$and τ_3, although they had the same value for the product $I_3\tau_3$. This result has suggested to us that PAS could be used as a tool to distinguish between samples which cannot be distinguished by conventional methods; such a tool could be particularly useful when the thermal history of a sample is not known, and it could make it possible to predict future aging of incompletely characterized samples. To pursue this idea, we have planned a series of measurements on samples of identical composition that are subjected to different thermal treatments that eventually bring them to the same temperature and the same free volume. We will run these measurements as part of the research program on our new contract.

4. We obtained preliminary results on a new technique that could provide additional information on the free volume distribution. This technique involves the simultaneous measurement of the positron lifetime and the momentum of the annihilated positron-electron pair. Annihilation of o-Ps, which provides information on free volume, involves a higher pair momentum than other modes of annihilation in the sample; therefore this type of measurement can lead to more definitive results in some situations. Our initial results (unpublished) show a clear difference between the high-momentum and low momentum lifetime distributions, with a much larger value of I_3 for the high momentum curve. These results were obtained over a period of six weeks, and they involved an accumulation of one million positron annihilation events. (In contrast, our lifetime apparatus normally accumulates one million events in about 15 minutes.) Clearly, higher efficiency is required, and we have begun to upgrade our momentum-lifetime apparatus, as described in our latest progress reports, to improve its efficiency.

5. We have begun a study of stress effects. We have prepared a holder that will allow us to measure positron lifetimes in a sample that is stretched by a precisely determined amount. This will allow us to investigate the positron lifetime distribution as a function of the applied stress and the length of time that the stress has been applied. Our preliminary results indicate that stress effects are easily observable by PAS. This work is continuing on our new contract.

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