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FAILURE ANALYSIS FOR POLYCARBONATE
TRANSPARENCIES



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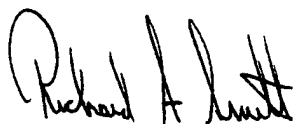
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PREFACE

An attempt was made to provide a correlation between physically induced *aging* and PALS based on theories that state that physically induced aging is due directly to changes in free volume. That is, external factors such as time, temperature, stress, environmental conditions et cetera can cause changes in free volume and at sufficient levels these external factors can affect physical aging leading to embrittlement of a bulk material. Since it was proposed that aging is solely dependent on free volume changes, the manner in which the free volume changes occur should be irrelevant. Therefore, for every free volume state there should be one and only one associated physical response (physical response is being defined by a material's tensile stress-strain relationship), regardless of exposure history. If this were true a correlation between the free volume and physical response could have been developed and used to determine the proximity to the ductile-brittle transition point.

PALS and tensile testing results will show that a unique free volume state could be reached from several aging conditions and that for these conditions several physical responses could also occur. It is not surprising that unique physical responses would be created from different combinations of exposure or that a unique free volume state could be reached from different exposures. However, according to the tested theory, different physical responses should not occur for single free volume state and the reverse situation of different free volume states having a single physical response is also contradictory to the cause and effect relationship proposed. Both of these relationships were found.

The goal of this program was to identify the postulated one-to-one free volume-tensile correlation that does not appear to exist based on the accumulated data. Therefore, the focus of this report beyond the review of the data is to review the preliminary theory and to briefly discuss alternative theories which may better explain the apparent lack of the desired correlation. It is our belief that theories which attribute changes in free volume to a response to and not a cause of aging is best supported by the accumulated data. These theories claim that the apparent cause and effect relationship on which this program was proposed often occurs as a coincidence of free volume changing concurrently with the true mechanisms of aging.

Attempts were made to identify coincidental correlations between free volume and exposure and physical response and exposure. These correlations could provide insight into how both free volume and physical response changes even if the two factors are not directly related. There were indications that free volume did have a strictly increasing or decreasing response to several of the exposure factors when the exposure factors were examined independently. However, the test matrix was initially established assuming only the two dependent variables of free volume and physical response. Therefore, the matrix was not large enough to allow for determination of a correlation for the additional dependent factors of time, temperature and loading with either free volume state or physical response. This reduced the examination of the data to how it supported or contradicted present theories on aging and free volume.

Failure Analysis for Polycarbonate Transparencies

1. INTRODUCTION

The goal of this program was to assess the feasibility of using positron annihilation lifetime spectroscopy (PALS) as a diagnostic, preventive, and predictive methods for the analysis of polycarbonate fracture based on the model of a critical free volume leading to a brittle-ductile transition. Since it has been shown that polycarbonate can be rejuvenated by reheating above its glass transition temperature and requeenching to regenerate the necessary excess free volume, brittle failures can be averted in transparencies that are close to the ductile-brittle transition.

2. BACKGROUND

There are currently no known acceptable nondestructive testing procedures which can accurately predict the onset of embrittlement of polycarbonate used in aircraft canopies due to aging. Since it has been theorized that aging is synonymous with changes in free volume, then the level of aging possibly could be quantitatively measured using positron annihilation lifetime spectroscopy (PALS). A correlation could then be drawn between the level of free volume and the degree of embrittlement in polycarbonate transparencies. This would then lead to a method of using PALS to identify the critical free volume which would indicate the onset of brittle failure.

It is known that free volume changes are often seen after exposure to time, temperature and stress. However, the relationship between cause and effect of free volume and aging has not been thoroughly examined. There are several models regarding aging and changes in free volume that will be discussed later. Free volume as a result of aging and not a cause could provide the desired correlation if the changes in free volume occur in the same time frame as the changes in tensile properties. However, if the changes in free volume lag the changes in tensile properties then a correlation could only be determined by looking at each possible influence of aging and determining the amount of time required for the sample to reach free volume equilibrium for the given exposure. Even identification of the rate to equilibrium would not provide a one-to-one free volume relationship, but would instead allow for the creation of a series of curves that would correlate free volume to aging for a given exposure. This would then require that the precise history of exposure of each sample be known.

Real time aging of polycarbonate is a slow process which could not be incorporated into a practical test program. Therefore, *aging* will be defined as the exposure of polycarbonate samples to external factors of time, elevated temperatures and loads. These factors were selected to introduce changes in the physical response and the free volume of the polycarbonate. Changes in response would be manifested as differences in tensile yield stresses and tensile yield strains. The change in the free volume would be seen as a change in either the number of sites or average size of sites. The product of the last two parameters is postulated to be proportional to the total free volume in the examined sample.

3. TEST PROCEDURES

3.1 Sample Exposure

A matrix of exposure conditions was created to determine if for a given free volume state there exists a respective tensile state. A range of exposure was selected so that coincidental correlation could be avoided. Table 1 shows the exposure matrix. All samples shown in this table were created from annealed polycarbonate that was heated to 250F for one hour and then allowed to equilibrate to room temperature slowly. Samples were routed from 1/8" sheet stock into 1/4" width tensile bars. Holes were drilled into the grip section for the application of the stress.

Initially, samples were to be tested using 1/2" thick tensile bars. Unfortunately, to obtain the desired stress levels the loading requirements were prohibitive. However, examination of the 1/2" samples was desired, as this is a commonly used material thickness. Therefore, the matrix shown in Table 2 was also established for the thicker samples without the inclusion of a stress factor.

Due to space limitations samples could not be exposed consecutively. The three-month samples were exposed to the required temperature in ovens while dead weights were hung onto the samples using S-hooks. When the three-month samples were removed, they were immediately replaced with the six-month samples. Time requirements made it necessary to have the remaining nine-month samples exposed at the creep lab of the Advanced Materials Engineering Experiment Station at Michigan State University.

3.2 Sample Testing

The PALS samples were tested at 70F. Humidity conditions were not recorded. Samples were placed in a controlled temperature and humidity room when not being tested via PALS. Spectrum collection took approximately ninety minutes and five spectra were collected per sample. Therefore, only two samples could be tested per day. Samples were placed in a holder that registered the location of the tested area.

Table 1: Exposure Matrix

Aging Temperature (C)	Stress Level, MPa (lbs.)	Exposure Period (months)	Samples Exposed/Period	PALS Values	Tensile Values
25	0	0, 3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
25	7 (30)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
25	14 (60)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
25	21 (90)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
50	0	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
50	7 (30)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
50	14 (60)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
50	21 (90)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
75	0	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
75	7 (30)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
75	14 (60)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
75	21 (90)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
100	0	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
100	7 (30)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
100	14 (60)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
100	21 (90)	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain

Table 2: Exposure Matrix (thick samples)

Aging Temperature (C)	Stress Level, Mpa (lbs.)	Exposure Period (months)	Samples Exposed/Period	PALS Values	Tensile values
25	0	0, 3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
50	0	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
75	0	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
100	0	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain
125	0	3, 6, 9	2 pals, 3 tensile	I3 and τ 3	Yield Stress, Strain

It was expected that there would be some variations due to stress gradients from the loaded samples and to a lesser degree from temperature exposed samples. It is impractical due to the nature of the samples to create perfectly symmetrical stresses. This could cause the measured PALS results to be based on areas of slightly different regions of stress, while the tensile results of the sample as a whole may appear to be identical. The use of a sample holder designed to register the PALS measurement device to the sample was used to help minimize this issue and the use of several samples should help average the influence of local variation.

4. POSITRON ANNIHILATION SPECTROSCOPY

Basic research in positron annihilation spectroscopy (PAS) techniques spans a period of more than four decades. Initially, interest in these techniques was confined to the fields of chemistry and physics. However, when work performed in the 1960's demonstrated these techniques were sensitive to defects and vacancy structures in metals, the application of PAS techniques in the applied sciences was popularized. Early efforts demonstrated PAS techniques to have the unique ability to distinguish between vacancy and dislocation type defects in metals; a sensitivity to vacancy defects of the order of parts per million, and an ability to characterize the size of vacancy defects, including mono or di-vacancy structures and void formation. The application of PAS to the study of polymers gained popularity as a result of a number of works published in the 1970's which demonstrated the sensitivity of PAS techniques to free volume. One of the first reviews of PAS in polymer science was published in 1973, by Hamielec, et al.¹ Armed with the conventional wisdom of free volume theory and a new tool capable of directly characterizing free volume in polymers, polymer scientists began to publish a number of revealing works in the 1980's and 1990's which provided new insight into polymer morphology and polymer behavior.

A thorough review of the physics on which PAS techniques are based is not presented. Likewise, neither is a complete description of the applicability of these techniques to the study of polymers. The reader is referred to several articles for a more thorough explanation of PAS theory and applications.^{2,3,4,5} In this document, only the basic theory on which these methods are based is presented to familiarize the reader with the experimental concepts. Emphasis is placed on reviewing the application of PAS techniques to the study of polymers and polymer matrix materials.

¹A.E. Hamielec, et al., *J. Macromol. Sci. - Rev. Macromol. Chem.*, C9(2), P.305, 1973.

²J. Stevens, *Methods of Experimental Physics*, Vol. 16 A, p. 371, 1980.

³J. Jilek, *Progress in Organic Coatings*, 5, p. 97, 1977.

⁴A. Varisov, et al., *Russian Chemical Reviews*, 50 (10), p. 991, 1981.

⁵C. Coleman, et al., *British Polymer J.*, 15, p. 56, 1983.

4.1 Positron Annihilation Spectroscopy Techniques

The basic nuclear phenomenon on which PAS techniques are based is the interaction and annihilation of positrons with electrons. The positron is the *antimatter* particle of the electron, sharing similar physical attributes with the notable exception that the positron is positively charged. As might be expected, positrons are short lived in the real world because they annihilate with electrons; the combined masses of the positron and the electron are carried off in the form of energy (gamma rays). Positron annihilation spectroscopy techniques are based upon the interaction and annihilation characteristics of positrons with electrons in matter. There are three basic PAS techniques, each utilizing different pieces of information about the positron/electron annihilation event to discern information about the local environment in which the interaction occurs:

- Positron annihilation lifetime spectroscopy (PALS)
- Doppler broadening spectroscopy (DBS)
- Angular correlation of annihilation radiation (ACAR).

All three techniques are represented schematically in Figure 1. The present investigation employed the technique of positron annihilation lifetime spectroscopy (PALS).

In a typical PAS experiment, the positron source, usually a decaying isotope such as Na-22, is placed between two identical samples being characterized. Upon decay of the isotope, a positron and a high energy 1.28 MeV gamma ray are emitted simultaneously. The energetic positron is injected into the sample where it dissipates its energy through a series of elastic and inelastic collisions in a process termed *thermalization*. Once the positron thermalizes, it will drift through the lattice, typically sampling a volume of the order of 2000 Angstroms in diameter before annihilating with an electron. Because of the positive charge of the positron, the drifting positron will preferentially be drawn to areas where there is a net negative charge and will be repelled from areas of high positive charge. The implications of this are that positrons will rarely annihilate with electrons which are strongly bound to lattice atoms because of charge repulsion. Instead, positrons will preferentially annihilate in regions where the electron density is relatively low, including defect sites, or neutral or negatively charged vacancies and voids.

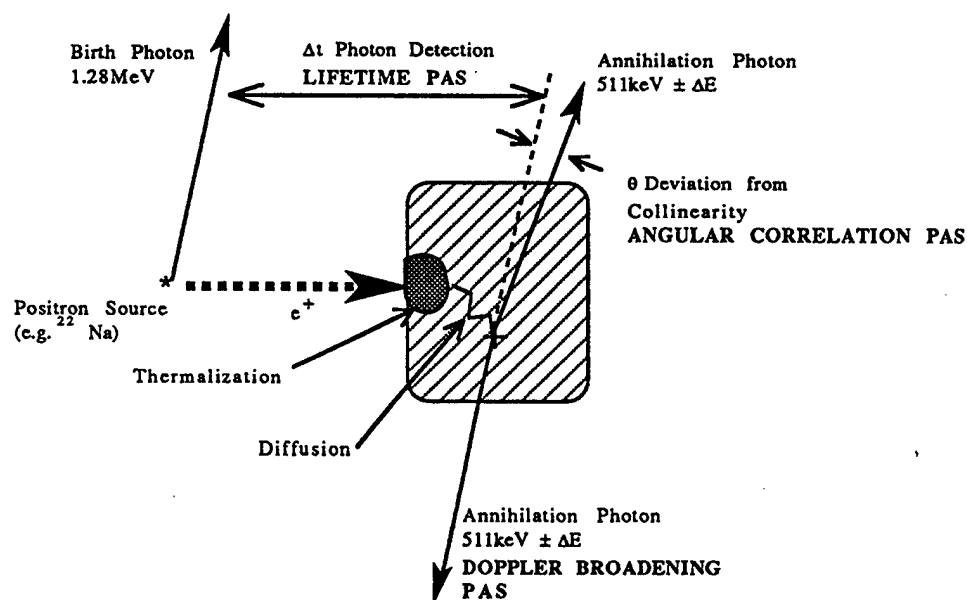


Figure 1. Schematic representation of positron annihilation spectroscopy techniques.

Annihilation occurs when there is an overlap between the wave functions of the positron and an electron encountered by the positron. Under ideal conditions (rest mass and energy), the mass of the two annihilating particles is carried off in two detectable 511 keV gamma rays emitted 180 degrees apart.

In molecular materials, there is a high probability that the positron will combine with an electron from the sample media, forming a complex known as *positronium*. Positronium is similar to a hydrogen atom, with the positron serving as the nucleus of the atom. Positronium exists in two states: para-positronium (p-Ps) in which the spins of the positron and electron are antiparallel, and ortho-positronium (o-Ps) in which the spins of the positron and electron are parallel. Para-positronium is very short lived, typically having a lifetime of the order of 125 psec, and shows no variation with temperature or structure. Ortho-positronium (which has a lifetime of 140 nsec in a vacuum) is much more stable, and has demonstrated a propensity for localizing in free volume cavity sites. As such, the annihilation characteristics of o-Ps are expected to reflect changes in the local free volume environment in which the

annihilation event occurs, and thus be sensitive to structural and physical changes occurring within the polymer material.⁶

PAS methods provide many benefits over other nondestructive methods of evaluation. PAS techniques are typically non-stimulating, and capable of ascertaining structural information without disrupting the physical state or structure of the sample being characterized. In addition, PAS techniques offer a distinct level of sensitivity because they monitor atomic level perturbations in structure that are not detectable by other techniques. Thus, PAS is capable of discerning structural characteristics or changes that may lead to failure well before these changes can be reflected by macroscopic property measurement differences or using current techniques for microstructural analysis. While PALS is applicable to the study of a wide range of organic and inorganic compounds (metallic and nonmetallic), this method is particularly useful in the characterization of polymeric materials because of its sensitivity to the free volume state of these materials. Free volume can be loosely defined as the volume within a polymer that is unoccupied by the molecules. Free volume is known to have a significant influence on the macroscopic physical properties of the polymer system. Traditional techniques of ascertaining free volume information are not capable of directly monitoring the free volume state of a system but must infer information about the free volume state by utilizing free volume interpretations of data which is believed to correlate with free volume content.⁷ PAS techniques, on the other hand, are directly sensitive to the free volume state of the system. Since PAS techniques provide a direct measure of free volume, conventional free volume theories can be used as a direct means for data interpretation. Some typical applications of PALS in polymer science are presented in Table 3.

4.2 Positron Annihilation Lifetime Spectroscopy (PALS)

In positron annihilation lifetime spectroscopy (PALS) the lifetime of the positron in a sample is characteristic of the local electron environment in which annihilation occurs. The positron lifetime is measured using picosecond timing equipment. A typical PALS system is presented in Figure 2. The lifetime of the positron is determined as the difference between the time of *birth* of the positron, and the

⁶W. Brandt, *Appl. Phys.*, 5, p. 1, 1974.

⁷K. Okamoto, et al., *Mat. Sci. Forum*, 105-110, p. 1675, 1992.

Table 3: Applications of PALS in Polymer Science.

<u>Materials Degradation</u>	<u>Material/Property Characterization</u>
<ul style="list-style-type: none"> • environmental (e.g. UV) • mechanical • thermal • chemical • physical aging 	<ul style="list-style-type: none"> • free volume • crystallinity • crosslinking • miscibility • secondary relaxations • hardness • microstructure • plasticizing effects • degree of cure/cure kinetics • interfacial characteristics (composites, coatings)
<u>Liquid-Polymer Interactions</u>	
<ul style="list-style-type: none"> • permeability • diffusion • absorption 	

time of annihilation. Photomultiplier tubes (PMTs) and energy discriminating electronics are used to determine each of these events. The 1.28 MeV gamma ray, which is emitted simultaneously with the positron during the decay process, is used to signal the birth of the positron and start the picosecond (psec) timing clock. The clock will run until one of the annihilation gamma rays (511 keV) is detected. The *lifetime* of the positron is then determined and stored on a multichannel analyzer (MCA) for subsequent analysis. A typical PALS spectrum consists of approximately 1×10^6 annihilation events (Figure 3). Data (gamma ray) collection efficiency is determined by the type of scintillator material used in the PMTs and the width of the windows set on the CFDDs (constant fraction differential discriminators), i.e., the manner in which the system is set up and calibrated. Once a system is calibrated, collection times for sample spectra varies according to sample type and dimensions, with sample thickness being the most critical parameter. Thicker samples separate the PMTs from the point source located at the center of the test geometry, decreasing the gamma collection efficiency in proportion to the square of the separation distance. With a sample thickness of the order of 1/8-inch, data collection times of as little as 15 minutes may be achieved with conventional positron sources, but data collection times of the order of 1 to 2 hours per spectra are more typical. Data collection time can be significantly improved using positron beam techniques, where positron fluxes of the order of 10^6 to 10^9 can be achieved. Regardless of the source configuration, for improved statistics, results are typically reported as the average of five to ten spectra collected sequentially on a given sample.

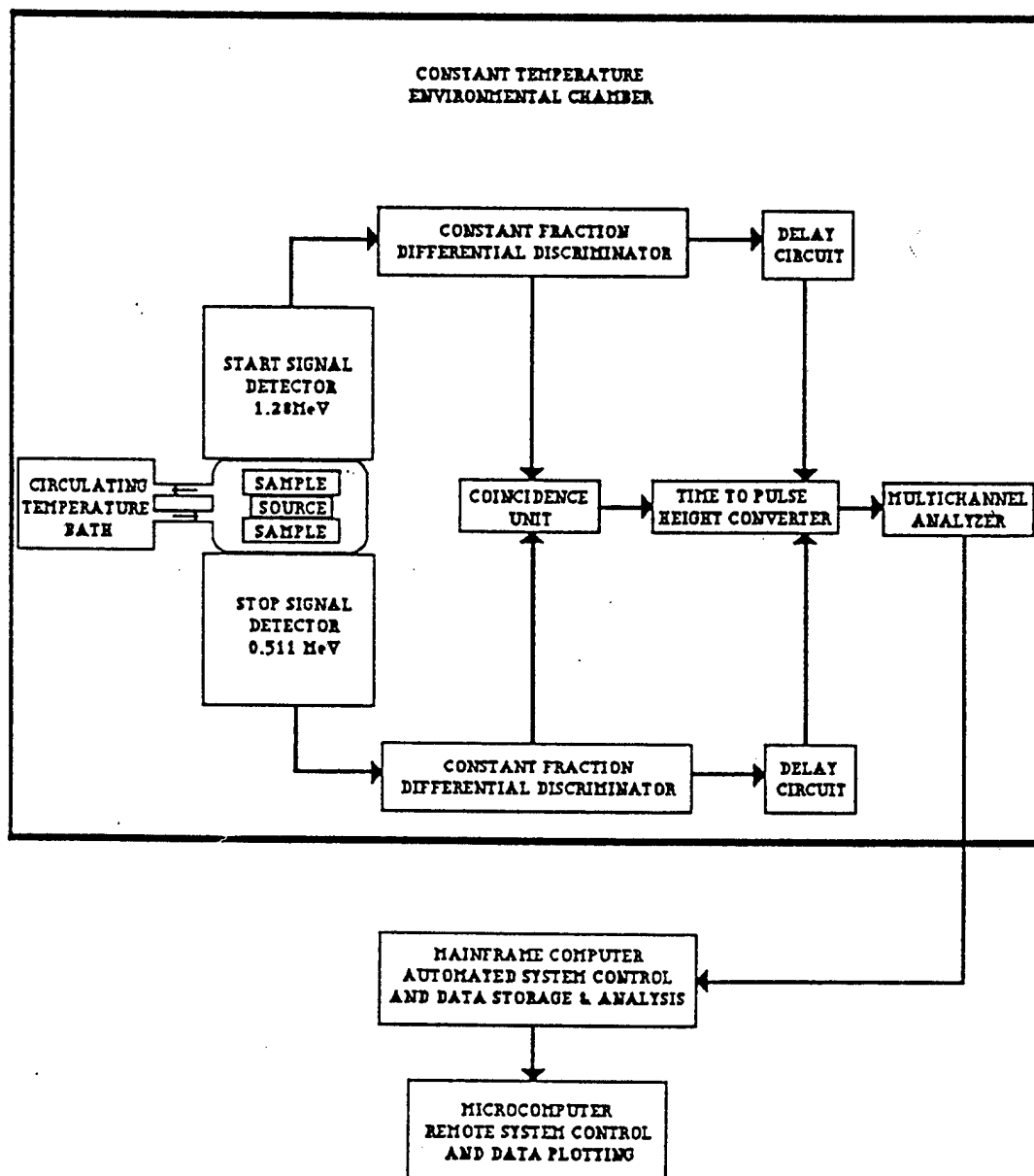


Figure 2. Schematic representation of a typical PALS system.

Typical PALS Spectrum

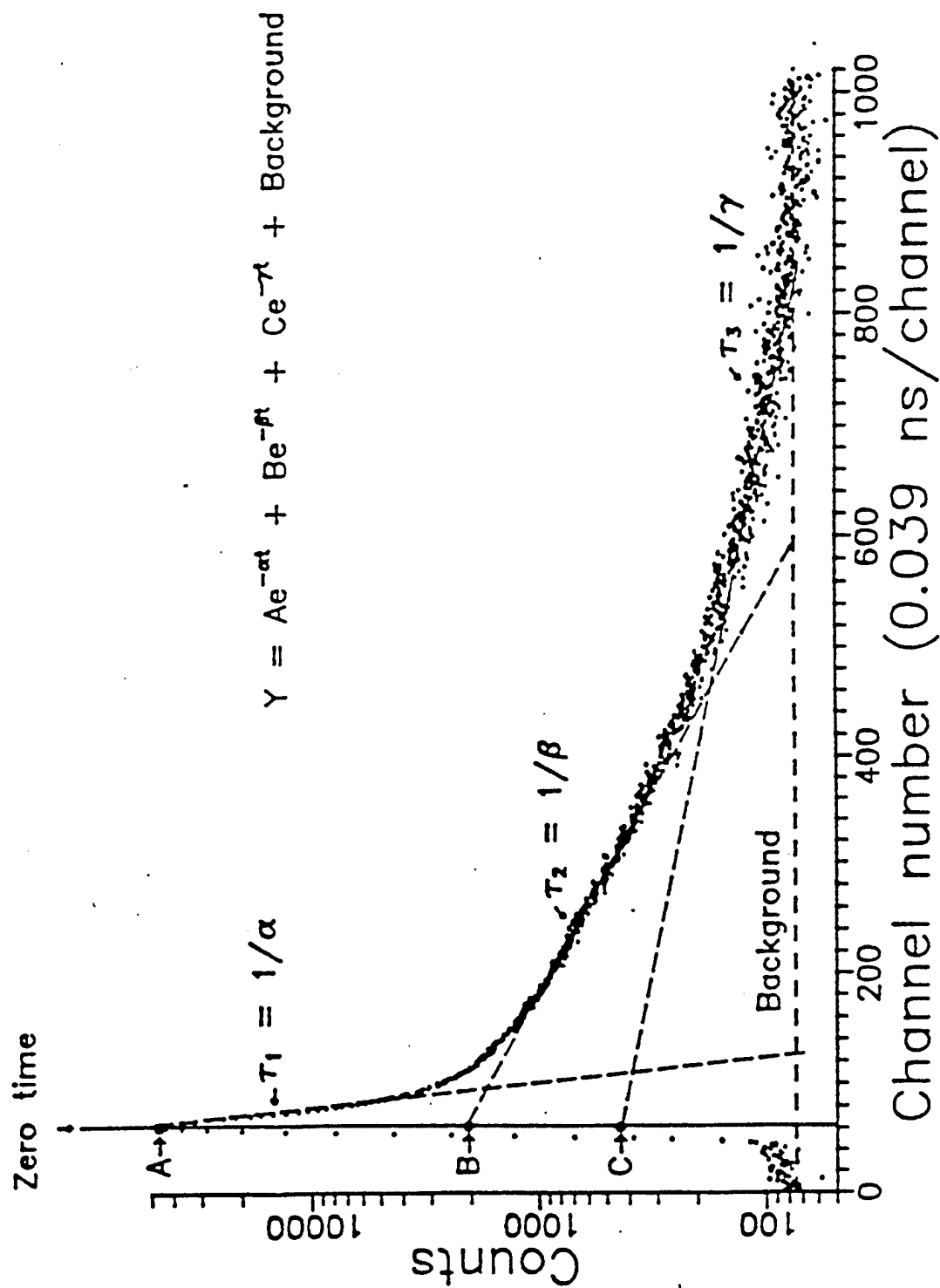


Figure 3. A typical PALS spectrum.

Lifetime data are extracted from the spectra by computational analysis. PALS spectra collected on polymer samples are typically deconvoluted into three or four decaying exponentials, the slopes of which are inversely proportional to the annihilation lifetimes of the positrons in the sample. The area under each slope (exponential tail) is proportional to the number of annihilation events which occurred with that particular lifetime (t_i). This value is reported as an intensity value ($\%I_i$). The first lifetime (τ_1) is typically associated with para-positronium annihilation events, assuming a constant value of approximately 125 psec. The second lifetime (τ_2) is typically referred to as the *bulk* lifetime, and is associated with the annihilation of free (unbound) positrons in the polymer. The third lifetime (τ_3) is associated with ortho-positronium annihilations, and is typically of the order of 1 to 3 nsec in polymers. Ortho-positronium lifetimes have been demonstrated to be directly related to the size of the free volume cavity in which annihilation takes place. The intensity of this component ($\%I_3$) has been correlated with the number of free volume cavity sites. PALS analysis of polymeric materials is dominated by interpreting changes in τ_3 and I_3 in terms of free volume theory. However, it should be noted that the $\%I_3$ (the number of ortho-positronium annihilations) is not only a function of the number of free volume cavity sites, but is also a function of the probability of positronium formation. Therefore, care should be taken when interpreting PALS data to ensure that the reported results properly reflect both of these contributions to $\%I_3$. This requires careful consideration of all of the PALS data, and the trends evident in this data, as well as careful experimental design to determine the factors that may affect the probability of ortho-positronium formation in the polymer system under investigation. In some instances, a fourth lifetime can be extracted from polymer data. This lifetime, typically of the order of 1.0 nsec is typically associated with source/surface annihilation events.

4.3 PALS Data Analysis

All of the PALS data presented in this work were fit using the deconvolution routine PFPOSFIT. All of the data are reported as the average and standard deviation of at least five spectra collected consecutively on each test sample. Data analysis was performed in an iterative fashion to achieve the best fits to the spectra. All data were fit as the sum of three decaying exponentials (three lifetime values). The best fits were typically obtained by: (1) fixing the shortest lifetime event to 125 psec, the lifetime of para-positronium (p-Ps) annihilation events; (2) accurately determining the time zero channel of the spectra, (3) accurately fitting the resolution function of the system; and (4) fitting the data with accurate initial lifetime estimates. Sound data analysis procedures are crucial to the outcome of the

experimental results, as inaccurate estimates for the time zero channel lead to inaccurate determinations of lifetime intensity values, and inaccurate initial resolution and lifetime guesses can cause PFPOSFIT to iterate to a local minimum that does not accurately reflect the lifetime distributions of the spectrum.

Fixing the resolution function and/or the short lifetime component typically forces PFPOSFIT to separate the first and second lifetime components, resulting in a decrease in the standard deviation associated with the intensity of each of these components. While some may argue that this may skew the shorter lifetime data, it does make it easier to separate out "poor" spectra that are inconsistent with the other spectra in a given data set. Without fixing either of these values the standard deviation of the intensity values for the first and second lifetimes can be too high to allow these values to be of much use. Furthermore, for polymers the long lifetime component (ortho-positronium) is usually of the most consequence, and it is rare that differences in spectra would occur in the short lifetime data without more pronounced changes occurring in the long lifetime data.

A source correction factor for the titanium encapsulate used for the Na-22 source was determined based on spectra for annealed and polished copper. However, it was not used in the final data analysis for the simple reason that the goal of the program was to identify relative changes between samples within a given sample set, so the contribution of source annihilations would be normalized. The use of a source correction factor tended to complicate the data analysis unnecessarily, as it is often difficult to accurately determine the appropriate source correction factor when investigating polymers. The reason for this is related to the difference in work function associated with the pure metal standard (e.g. copper) and organic materials. Since metals have a higher work function, there is a greater probability the injected positrons will diffuse back to the surface and annihilate in the source or at the source/sample interface. The probability of this occurring is very low in polymers, so a source correction factor determined for the metal would provide an unnecessarily high estimate for polymer samples.

In most cases, better fits of the spectra within a given data set decreased the standard deviation of the data within that data set. However, the relative difference between samples within a given data set was affected very little by the "goodness of fit" determined by PFPOSFIT. The primary reason for this is that the long lifetime of ortho-positronium is far removed from the two shorter lifetime values, and is therefore more easily separated by the deconvolution routine. Even so, due to the inexact nature of the lifetime extraction routines, and the experimental variables that can affect data collection and the resultant spectral output, it was not always possible to obtain a reasonable fit to the PALS spectra. In most instances, these spectra can be identified by some anomaly in the spectral output, and can be eliminated from the data set. However, in some instances, good fits were obtained for spectra that demonstrated obvious differences from

the other spectra in a given data set. For example, tau-3 may have iterated to a noticeably different lifetime, causing a shift in the spectral intensity values away from the average of the other spectra. Spectrums that could be clearly distinguished from the other data were also eliminated from the sample data sets reported.

5. POLYCARBONATE

Polycarbonates are tough, transparent polymeric materials that have been a valuable part of the family of engineering thermoplastics since their introduction into the commercial market in the early 1960's. Favorable properties such as structural rigidity, toughness, and good dielectric strength, have made polycarbonate resins a popular choice for applications in the electrical and automotive industries, and many other industrial and commercial applications. The polycarbonate tested under this program, is representative of polycarbonate grades used in the manufacture of aerospace transparencies.

The most commercially significant polycarbonate resins are based on the monomer bisphenol-A (2,2 bis (4-hydroxyphenyl) propane). Molecular weights of the order of 30,000 are typical. Polycarbonate will not readily crystallize under typical manufacturing conditions but will form an amorphous polymer that exhibits a high degree of short range order and regularity.⁸ Although crystalline polycarbonate can be achieved in solvent cast films, crystallization in the bulk generally is prohibited by the rigidity of the polymer backbone, as attributable to the stiff phenylene groups and the length of the repeat unit.⁹ These same factors also contribute to the rather large fraction of retained free volume in polycarbonate and its relatively high glass transition temperature (T_g) of approximately 145 C as determined by DSC and dilatometry.^{10,11}

Structural as well as free volume arguments have been developed to explain a number of secondary relaxations in polycarbonate below its T_g (glass transition).^{12,13} Most significant of these are

⁸H. Schubach and B. Heise, *Coll. Polym. Sci.*, 264 (4), p. 335, 1986.

⁹W. Christopher and D. Fox, Polycarbonates, Reinhold Publishing Co., N.Y. 1981.

¹⁰Y. Ishida and S. Matsuoka, *J. Polym. Sci., Part B*, 3, p. 321, 1965.

¹¹G. Locati and A. Tobolsky, eds., Advances in Molecular Relaxation Processes, Elsevier, Amsterdam, p. 375, 1970.

¹²S. Matsuoka and Y. Ishida, *J. Polym. Sci., Part C*, 14, p. 247, 1966.

¹³D. Hull and T Owen, *J. Polym. Sci.*, 11, p. 2039, 1973.

the existence of a β transition in the vicinity of 0-85 C and a low temperature γ relaxation peak between -50 and -100 C.^{14,15} The β transition reflects the existence of local motions within the polymer main chain and is indicative of the large amount of free volume quenched into the sample as it is cooled through the glass transition. The γ relaxation peak is usually attributed to motions of the phenylene groups in conjunction with motions of the carbonate group, or with the methyl groups on the pivotal carbon of the isopropylidene chain, or a collective motion among all three constituents.^{11,16} Excess free volume and the existence of these low energy secondary transitions have been correlated with the high impact strength and ductile behavior of polycarbonates.^{11,13,17}

Polycarbonate is generally described as exhibiting a planar, zigzag structure, and existing in two conformational structures: *trans-trans* and *trans-cis*; the *cis-cis* structure being precluded by severe overlap between neighboring phenylene rings.^{18,19,20} Of particular importance in determining the equilibrium structure of polycarbonate and the concomitant structure-property relationships are: (1) the relative energy difference between the two conformational states of polycarbonate; (2) the cooperative motions among the segments that allow these conformational changes to occur and for energy to be absorbed; and (3) and any relevant free volume fluctuations. The *trans-trans* conformational state of polycarbonate is preferred to the *trans-cis* state, since the *trans-trans* state is the lowest energy conformational state, exhibiting the highest degree of order.¹⁷

Molecular motions responsible for the transition between the two conformational states have been modeled by Jones.¹⁹ The fundamental motion described in this model is the exchange of a *trans-cis* conformation of the carbonate with a *trans-trans* conformation of a neighboring carbonate. This exchange occurs by rotations about one of the C-O bonds in each of the two neighboring/participating

¹⁴K. Pathmanathan, et al., *J. Polym. Sci., Part B*, 27, p. 1519, 1989.

¹⁵C. Bauwens-Crowet and J. Bauwens, *Polym.*, 24, p. 921, 1983.

¹⁶J. Bicerano and H. Clark, *Macromol.*, 21, p. 585, 1988.

¹⁷S. Sacher, *J. Macromol. Sci., Phys.*, B9 (1), p. 163, 1974.

¹⁸E. Turska, et al., *Polym.*, 29, p. 321, 1979.

¹⁹A. Jones, *Macromol.*, 18, p. 902, 1985.

²⁰A. Tonelli, *Macromol.*, 5 (5), p. 558, 1972.

carbonate groups with concurrent rotation (flipping) of the phenylene groups attached to the other side of the carbonate groups opposite the C-O axis of rotation. The p flips of the phenylene groups are a result of inter- as well as intramolecular coupling.¹⁹ Artifacts of the proposed model are that (1) chain ends do not have to translate, (2) bisphenol-A units of the polymer chain outside of the two carbonate groups are not significantly reoriented except for the p flips, and (3) the bisphenol-A unit between the two participating carbonates is only slightly translated and reoriented.

Jones has suggested that this crankshaft-type segmental motion, in addition to free volume defects quenched into polycarbonate upon cooling through the glass transition, could provide a mechanism by which the ductility and high impact strength of polycarbonate could be explained. According to the model presented by Jones, localized strain is allowed to diffuse down the chain to a large volume defect at which point larger scale motions, comparable to those that may occur at the glass transition, could take place to dissipate the strain energy. As these volume defects are relaxed out by annealing (aging), the larger scale motions are prohibited and the strain is not readily dissipated. Hence, even though there may be a sufficient amount of free volume available for translational motion to occur, energy dissipation is hindered in aged samples due to a decrease in free volume defects, and less ductile behavior is exhibited.

Estimates of the order of 0.6 to 2.0 kcal/mol have been reported as the energy difference between the ground states of the two conformations, with 1.3 kcal/mol most often cited.¹⁶ The energy barrier separating the two states is reported to be of the order of 2.0 to 3.4 kcal/mol.^{16,19} Taking the relative energy differences into account, Bicerano and Clark used statistical methods to determine the population of *trans-cis* conformations to be approximately 24% at room temperature and argued that this population was sufficient to enable *crankshaft-type* cooperative motions within the polymer chain described by Jones.¹⁶

Through the work of Jones¹⁹ and Bicerano and Clark¹⁶ a model can be developed that explains the ductility of polycarbonate in terms of the population of *trans-cis* vs. *trans-trans* conformations. In the as-annealed state, the ductile behavior of polycarbonate may be attributed to a sufficient population of high energy *trans-cis* conformations and enough available free volume for energy dissipation to occur via the crankshaft motion proposed by Jones. However, the natural tendency will be for the structure to be driven from the high energy *trans-cis* state to the lower energy *trans-trans* conformational state, which exhibits more order and hence better structural packing. Thus, as a function of time, the population of *trans-cis* conformations will decrease as the population of *trans-trans* conformations increases. This process not only inhibits molecular mobility by decreasing the population of high energy

states that can absorb energy by transitioning to a lower energy state, but it also has a net negative effect on the available free volume that allowed this process to occur in the first place. This combination of events can be used to explain the ductile to brittle transition exhibited by many amorphous polymers as a function of aging time or low temperature exposure, as well as many aspects of the *physical aging* phenomenon.

6. THEORETICAL CONCEPTS

6.1 Thermodynamic Aspects of the Glass Transition

Several factors have been noted to contribute to the behavior of amorphous materials in the glass transition region. Of primary importance is cooling rate. As depicted in Figure 4 at temperatures above the glass transition region, molecular motions in the polymer melt occur at such a frequency that all molecular segments are able to maintain their thermodynamic equilibrium conformational structure and packing density. In this region the properties of the system may be described simply as a function of temperature and pressure (atmospheric pressure in this case).²¹ Upon cooling through the glass transition region, a departure from the equilibrium liquid structure occurs when the rate of the slowest structural rearrangement (relaxation) is of the same order as the rate of cooling.²² At this point, large-scale molecular motions become slow relative to the time scale of the vitrification process and are no longer able to respond to the changing temperature.²³ As a result, these motions are frozen out and a departure from the liquid equilibrium property-temperature curve occurs. As this departure is rate dependent, the transition occurs sooner in systems that are cooled at a faster rate through the transition region. This results from an increasing number of longer term relaxation processes that are unable to proceed to their equilibrium state within the time frame of cooling.²¹

If the transition temperature of the glass is taken as the point of departure from equilibrium, glasses that are formed during faster cooling will be characterized by higher glass transition temperatures.²³ Additional cooling below the glass transition region, causes these systems to remain further from the equilibrium liquid-like state of the glass; depicted in Figure 4 by extrapolating the equilibrium liquid-temperature line from above the glass transition to temperatures below the transition. In effect, the resultant glass may be considered to be a super-cooled liquid, retaining excess a function of temperature and pressure (atmospheric pressure in this case).²⁴ Upon cooling through the glass

²¹M. Tant and G. Wilkes, *Polym. Eng. Sci.*, 21 (14), p. 874, 1981.

²²A. Kovacs, et al., *J. Polym. Sci. Phys.*, 17, p. 1097, 1979.

²³M. DeBolt, et al., *J. Amer. Ceram. Soc.*, 59 (1-2), p. 16, 1976.

²⁴M. Tant and G. Wilkes, *Polym. Eng. Sci.*, 21 (14), p. 874, 1981.

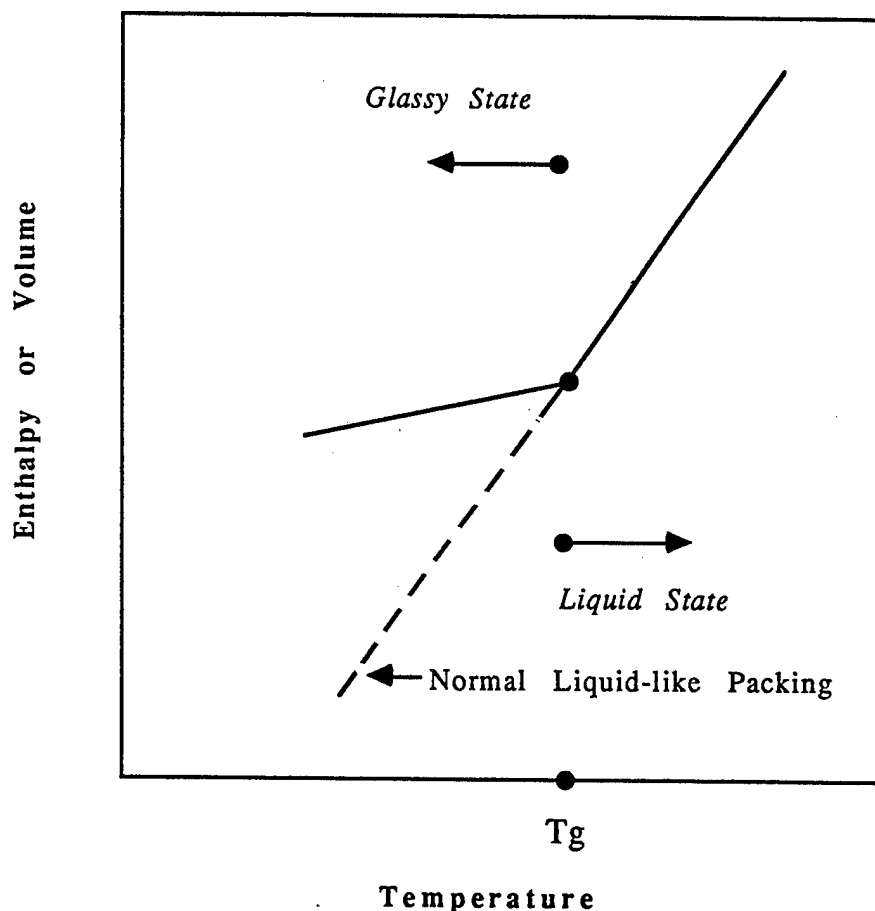


Figure 4. Schematic representation of the glass transition.

transition region, a departure from the equilibrium liquid structure occurs when the rate of the slowest structural rearrangement (relaxation) is of the same order as the rate of cooling.²⁵ At this point, large-scale molecular motions become slow relative to the time scale of the vitrification process and are no longer able to respond to the changing temperature.²⁶ As a result, these motions are frozen thermodynamic properties. As such, the properties of the glass in regions below the glass transition can no longer be described solely in terms of temperature and pressure. Additional characterization in terms of the instantaneous structure of the glass is necessary, as the properties and structure of the glass now have the capacity to change as a function of time.²¹

²⁵A. Kovacs, et al., *J. Polym. Sci. Phys.*, 17, p. 1097, 1979.

²⁶M. DeBolt, et al., *J. Amer. Ceram. Soc.*, 59 (1-2), p. 16, 1976.

It is important to note that the shape of the cooling curve does not change, but merely shifts to lower temperatures as the rate of cooling decreases and a greater amount of relaxation is allowed to take place in the same interval of time within the transition region.²³ This behavior is indicative of the thermorheologically simple behavior that glasses exhibit during structural relaxation implying that although the displacement of the curve along the time or temperature axis may shift, the shape of the curve will remain constant.²²

If the cooling rate through the glass transition range is held constant, the effects of pressure on the vitrification process of the glass may also be assessed.^{24,25} Increasing the pressure raises the vitrification temperature so that upon cooling, the resultant glass departs from its equilibrium liquid structure at higher temperatures. Consequently, glasses cooled under pressure are characterized by higher glass transition temperatures.²⁵ This behavior is exemplified in Figure 5.

It is important to note that glasses vitrified under pressure result, as expected, in an increase in density relative to glasses formed under atmospheric pressures. Struik²⁹ noted that the volume change upon densification may exceed the decrease in free volume that accompanies physical aging by 1 to 2 orders of magnitude, yet the densification has little effect on the mechanical relaxations of the glass at temperatures below T_g . This behavior seems to contradict the free volume concept of physical aging as the initial state of free volume is a function of cooling rate. However, if the effects of aging are assessed in terms of the changes in relaxation time, and these changes, in turn, are attributed to changes in free volume, then the effects of cooling under pressure can be explained if cooling under pressures at a constant rate of cooling results in glasses with the same initial relaxation times. Struik's argument would favor the conformational argument presented in the previous section.

Although the actual mechanism by which this occurs is open to discussion, it is reasonable to assume that the effects of the decrease in free volume may be offset by the increase of longer relaxation time mechanisms available as a result of the higher T_g associated with cooling under pressure. The net result being a glassy system that exhibits similar mechanical relaxation behavior.

²⁷A. Weitz and B. Wunderlich, *J. Polym. Sci.*, 12, p. 2473, 1974.

²⁸W. Prest, et al., *Polym. Eng. Sci.*, 21 (18), p. 1181, 1981.

²⁹L. Struik, Physical Aging in Amorphous Polymers and Other Materials, Elsevier Scientific Publishing, New York, 1978.

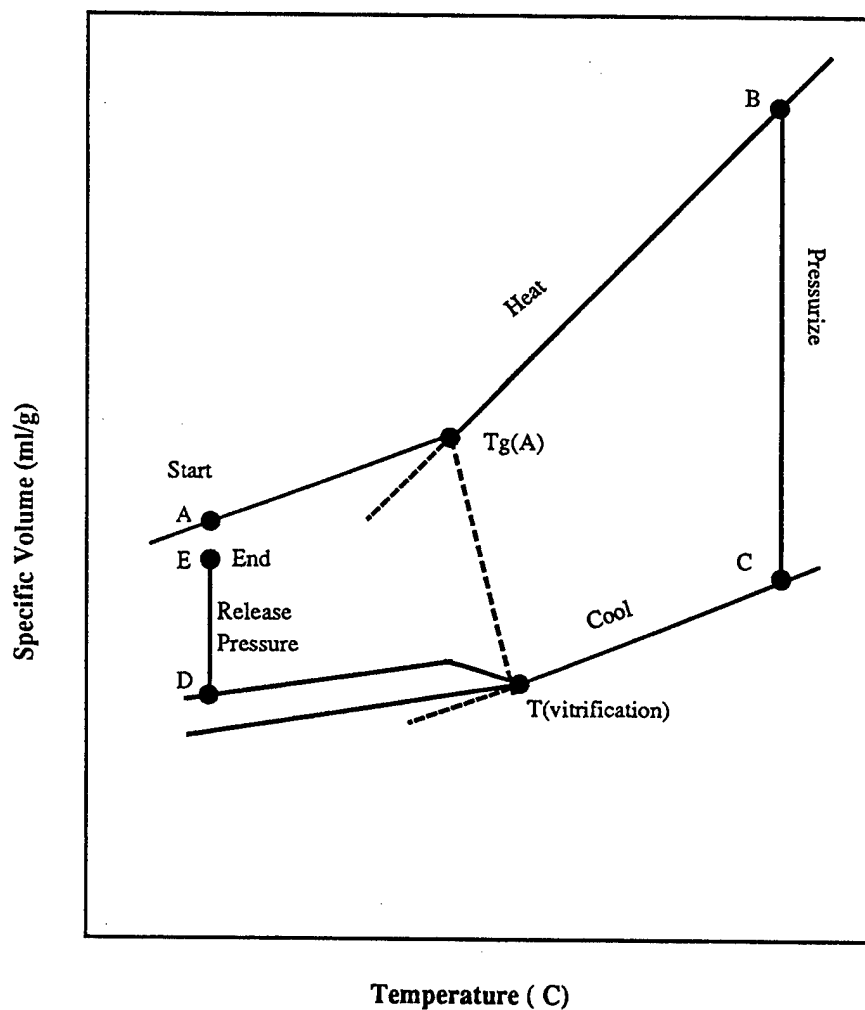


Figure 5. Schematic representation of the effects of pressure on the glass transition temperature.

The question still remains whether the behavior of the glass below T_g is expected to follow similar behavior as quenching the glass at faster cooling rates as both of these glasses may retain higher quantities of excess thermodynamic properties with respect to temperatures below T_g .

6.2 Physical Aging

As discussed in the previous section, upon cooling through the glass transition range the glass attains a structure that is no longer in thermodynamic equilibrium. Furthermore, the departure from equilibrium is a function of vitrification pressure, cooling rate, and any subsequent thermal or mechanical treatment imparted during processing. The non-equilibrium nature of this structure manifests itself in excess quantities of enthalpy, entropy, and volume with respect to the theoretical equilibrium structure of the glass.²¹ As a result of this non-equilibrium structure there is a thermodynamic driving force for the glass to approach its equilibrium state as a function of time at temperatures below the glass transition.^{21, 22} In addition, as there is a finite level of molecular mobility below the glass transition, particularly at temperatures approaching T_g , the non-equilibrium structure is able to approach its equilibrium state via molecular rearrangement and increased packing.^{21,30} The rate of this approach is a complex function of time, temperature, and the degree of departure of the glassy structure from its equilibrium structure at the aging temperature. It is important to note the contribution of all three of these factors in determining the rate of physical aging.

6.3 Structural Relaxation and Physical Aging

As may be noted in the descriptions of structural relaxation in the glass transition range and the process of physical aging, a great deal of similarity exists between these two phenomena.³¹ Physical aging may even be considered a continuation of the glass formation that sets in at the glass transition.²⁶ The increased rate of aging at temperatures approaching the glass transition, as well as the elimination of aging effects above the glass transition, suggests a close connection between physical aging and the relaxations occurring at the glass transition, implying the two phenomena may be modeled in terms of similar arguments.^{21,27,28} Indeed both processes affect the temperature dependent properties of glassy materials in much the same manner and direction, but the effects of physical aging are only perceivable on a much

³⁰L. Struik, *Failure in Plastics*, Brostow and Corneliusen, eds., Hanser, New York, p. 209, 1986.

³¹I. Hodge and A. Berens, *Macromol.*, 15, p. 762, 1982.

greater time scale. These relaxations are accompanied by concomitant changes in the physical and mechanical properties of the glass. As aging proceeds the properties of the polymer glass are expected to change as follows: an increase in yield strength,^{32,33,34} post yield stress drop,³⁵ density,^{30,32} flexural stress,³⁶ viscosity, relaxation times,²⁷ and microhardness.³⁷ A decrease is expected in impact strength/fracture energy,^{13,31,33,38,39} ultimate elongation,³³ and creep compliance.²⁷ Spurious results have been found for the effects of aging on Young's Modulus.^{29,40} Of particular interest to polycarbonate is the ductile to brittle transition in fracture mode as a result of aging.^{31,35,36,38,39}

6.4 Temperature Range of Physical Aging

Struik defined the temperature range in which physical aging may occur as the region between T_{β} , the highest secondary transition, and the glass transition.²⁶ Above the glass transition, the molecular response is such that the molecules are able to relax into their equilibrium conformation and packing density. At the β transition, segmental mobility decreases significantly and the process of physical aging is no longer able to proceed. Below this transition, molecular motions may still exist, but are not of the type to affect the relaxation behavior of the polymer (presumably due to the fact that they no longer

³²K. Neki and P. Geil, *Macromol. Sci., Phys.*, B8 (1-2), p. 295, 1973.

³³C. Bauwens-Crowett and J. Bauwens, *Polym.*, 23, p. 1599, 1982.

³⁴D. Legrand, *J. Appl. Polym. Sci.*, 13, p. 2129, 1975.

³⁵G. Adam, et al., *J. Mater. Sci.*, 10, p. 1582, 1975.

³⁶J. Golden, et al., *J. Appl. Polym. Sci.*, 11, p. 1571, 1967.

³⁷F. Ania, et al., *J. Mater. Sci.*, 24, p. 2934, 1989.

³⁸L. Broutman and S. Krishnakumar, *Polym. Eng. Sci.*, 16 (2), p. 74, 1976.

³⁹B. Thakkar and L. Broutman, *Polym. Eng. Sci.*, 21 (3), p. 155, 1981.

⁴⁰M. Tant and G. Wilkes, *Polym. Eng. Sci.*, 21 (6), p. 325, 1981.

⁴¹C. Bauwens-Crowett and J. Bauwens, *Polym.*, 27, p. 709, 1986.

⁴²G. Pitman, et al., *J. Mater. Sci.*, 13, p. 2092, 1978.

result in a change in free volume), and hence cause physical aging.^{21,26} As experimental methods for detecting secondary transitions improve and new transitions are identified and labeled, this definition requires some additional clarification. For example, Struik defined the range of physical aging for polycarbonate to be -100 to 150 C. Using current methods (DMA and DLS) and terminology, -100 C is defined as a low temperature γ peak for polycarbonate. Between this transition and the glass transition temperature, it is currently well accepted that polycarbonate exhibits its highest secondary transition temperature in the 70 to 85 C range. This transition, identified by DLS, DMS, and PALS, is currently defined as the β transition in polycarbonate.^{12,14,17,19} The β transition reflects the existence of local main chain molecular motions in polycarbonate that may significantly affect the structure and free volume state of the polymer, and greatly affect molecular relaxations. An accelerated rate of physical aging may be expected to occur in polycarbonate (or any other polymer system exhibiting a high temperature secondary transition of this type) between this temperature and the glass transition. As previously discussed, the low temperature γ relaxation is usually attributed to motions of the phenyl groups in conjunction with motions of the carbonate group, or with the methyl groups on the pivotal carbon of the propylene chain, or a collective motion among all three constituents.^{11,16} Thus, in the context of Struik's definition, physical aging in polycarbonate may proceed in the temperature range between the γ peak and the glass transitions. When defining the low temperature range of physical aging in a particular system, it is important to identify the lowest secondary transition temperature at which structural relaxations occur that affect the relaxation characteristics of the bulk system.

6.5 Rate of Physical Aging

It has been demonstrated in the literature that the extent of enthalpy relaxation in the glassy state corresponds to the amount of structural relaxation, or physical aging, occurring below the glass transition. In addition it has also been demonstrated that the extent of enthalpy relaxation during physical aging is a function of the aging temperature; a greater extent of enthalpy relaxation being possible at temperatures further from the glass transition temperature.⁴³ As the total amount of enthalpy relaxation is less for samples aged at higher temperatures, samples aged at higher temperatures will reach

⁴³S. Petrie, *J. Macro. Sci.*, B12 (2) p. 225, 1976.

their equilibrium structure in a shorter amount of time.⁴⁴ The amount of enthalpy relaxation has been noted to increase with increasing annealing time, asymptotically approaching a limiting value that increases with decreasing aging temperature, again approaching a limiting value that may be defined by the second order transition temperature.⁴⁵ Thus, at constant aging temperature (T_a), relaxation time can be shown to be an exponential function of the displacement from equilibrium.⁴² The rate of enthalpy relaxation has also been shown to increase as a linear function of increasing aging temperature, passing through a maximum at $T_a < T_g$ then decreasing as the aging temperature approaches T_g .⁴⁶ This behavior is expected as it reflects a competition between the enthalpy change during relaxation of the glass toward equilibrium, which increases with decreasing temperature, and the kinetics of the relaxation process which decrease with decreasing temperature.⁴⁷ At any given temperature, the initial rate of aging can also be expected to be a function of prior thermal history. For example, samples cooled at a faster rate through the glass transition may be expected to relax faster as the initial structural state of the glass will be further from equilibrium. As a result, the number of segments (presumably a higher population of the *ductile* high energy *trans-cis* conformations) available to participate in the relaxation process will be greater and relaxation will proceed more readily.⁴⁸

6.6 Models of Physical Aging

Although the material properties that change as a function of aging are well defined, the mechanism(s) responsible for this phenomenon are highly debated. Currently, there are three mechanisms that are used predominantly in the discussion of physical aging:

⁴⁴A. Chan and D. Paul, *Polym. Sci. Eng.*, 20 (1), p. 87, 1980.

⁴⁵S. Petrie, *J. Polym. Sci., Part A-2*, 10, p. 1255, 1972.

⁴⁶I. Hodge and G. Huvard, *Macromol.*, 16, p. 371, 1983.

⁴⁷R. Straff and D. Uhlmann, *J. Polym. Sci., Polym. Phys.*, 14, p. 1087, 1976.

⁴⁸C. Moynihan, et al., *Polym. Eng. Sci.*, 24 (10), p. 1117, 1984.

- (1) the free volume model^{27,38,40,46,47}
- (2) the entanglement model^{48,49}
- (3) and a model based on changes in molecular configurations.^{50,51,52,53}

The most popular arguments for the mechanism of physical aging are given in terms of free volume. Struik, the major proponent of this model, describes the physical aging process in the following manner.^{26,27} Above the glass transition temperature, free volume and molecular mobility are large and are able to decrease with temperature down to the glass transition temperature. Below the glass transition temperature, free volume becomes small, molecular mobility is hindered, and the change in free volume is no longer able to follow the change in temperature. As a consequence, upon further cooling to a final temperature below the glass transition temperature, there is an excess amount of free volume frozen into the structure. Since there is still finite mobility at any given temperature below T_g , free volume will slowly decrease toward its equilibrium value as a function of time. As the free volume relaxes, the molecular mobility decreases proportionally, and all properties that depend on molecular mobility change accordingly. Thus, Struik proposes that physical aging can be associated with a gradual decrease in free volume. This decrease in free volume causes a decrease in molecular mobility or an increase in relaxation or response time. Struik also notes that the increase in response time is in direct proportion to the time spent at the aging temperature ($T_a < T_g$).

⁴⁹W. Browstow, Failure of Plastics, Brostow and Corneliussen, eds., Hanse, New York, p. 71, 1986.

⁵⁰M. Ali and R. Sheldon, *J. Appl. Polym. Sci.*, 14, p. 2619, 1970.

⁵¹D. Prevorsek and B. DeBona, *J. Macromol. Sci. Phys.*, B19, p. 605, 1981.

⁵²D. Turner, *Polym.*, 19, p. 789, 1983.

⁵³R. Buebeck, et al., *Polym. Eng. Sci.*, 24 (10), p. 1142, 1984.

⁵⁴R. Moore, et al., *Polym. Eng. Sci.*, 21, p. 903, 1981.

⁵⁵K. Neki and P. Geil, *Macromol. Sci., Phys.*, B8 (1-2), p. 295, 1973.

⁵⁶R. Haward, *J. Macromol. Sci. Rev. Macromol. Chem.*, C4, p. 191, 1970.

Conceptually, the free volume model provides a basis for interpreting the general aspects of physical aging and allows reasonable interpretations of the physical properties of aged materials based on the relationship between free volume and molecular mobility. Conventionally, free volume models demonstrated great success in explaining molecular response above the glass transition temperature. However, the popularity of the free volume model was largely due to the empirical success of the WLF (Williams, Landel, Ferry) equation,⁵⁷ which described the time-temperature superposition behavior of mechanical properties of polymers above the glass transition temperature, and the fact that this equation could be derived in terms of free volume terms from the Doolittle equation.³⁷ It should be noted that this equation was an empirical equation and never proved the validity of the free volume theory. Also, the extension of the WLF equation below the glass transition temperature is not possible since the system of interest is no longer considered to be in equilibrium. Thus, the extension of the free volume model below the glass transition temperature is further complicated, and the validity of applying in this range is questionable.

The major complications involved in interpreting changes in physical properties due to physical aging in terms of free volume are that it neglects thermally activated changes in conformations and entropy or any ordering that may take place during the aging process. Although these changes may result in a change in free volume that is in agreement with the concomitant changes in physical properties, interpretations of these property changes solely in terms of free volume would be incorrect. This would be particularly true if the size and distribution of free volume sites in the aged material were in excess of the quantities necessary for mobility. In such a case, arguments based solely on free volume could not possibly account for the changes that result in molecular mobility as a function of physical aging. Work by Bubeck and Bales supports this argument.⁵⁰ Based on their work, they suggested that free volume, as well as entanglement arguments, are inadequate in explaining the changes in the

⁵⁷M. Williams, et al., *J. ACS*, 77, p. 3701, 1955.

deformation properties of physically aged polymers. Bubeck and Bales,⁵⁸ in conjunction with Adam, et al.,³² and Haward⁵⁹ have further suggested that physical aging may be associated with local molecular conformational changes that, in conjunction with changes in local molecular packing, lead to a more ordered structure that is more prone to exhibit less ductile deformation properties.

6.7 Literature Review

Based on the initial arguments presented above, it is evident that the phenomenon of physical aging is not well understood and that a host of explanations have been proposed to describe the mechanisms responsible for physical aging. A review of the literature pertaining to this subject matter makes this observation even clearer. A vast amount of work has been performed on physical aging, most of which involves attempts to relate the physical properties of aged polymers to their thermodynamic properties, structure, and volume. A brief review of some of the literature in this area is presented. A general overview of this phenomenon can be found in works of Tant and Wilkes³⁷ and Struik.^{26,27}

Struik has studied the effects of physical aging on the mechanical properties of a large number of plastics and organic glasses and has found aging behavior to be a very general phenomenon.^{26,27} By drawing correlations between specific volume measurements and creep compliance results, both obtained as a function of aging time at temperatures less than the glass transition temperature, Struik formulated a theory based on free volume and its effects on molecular mobility to explain the physical aging process.

Legrand³¹ was the first to note the ductile to brittle behavior of polymers upon annealing. Legrand performed detailed mechanical tests on polycarbonate as a function of aging time in which the effects of the ductile to brittle transition were seen in tensile tests results as well as in Izod impact data. Corresponding density data were shown to increase as a function of aging time to a limiting value. Theoretical considerations of free volume decrease as well as entropy considerations were explored in terms of their effects on mechanical properties and the ductile to brittle transition resulting from aging. Combined with Struik's model of physical aging, Legrand's work contributed the piece necessary to draw correlation's between a *critical free volume level* and ductile to brittle transition behavior.

⁵⁸R. Bubeck and S. Bales, Order in the Amorphous State of Polymers, R. Miller and J. Rieke, eds., Plenum, New York, p. 347, 1987.

⁵⁹R. Haward, et al., *Colloid. Polym. Sci.*, 258 (6), p. 258, 1980.

Allen, et al.⁶⁰ confirmed the results of work performed by Legrand by measuring Izod impact strength and loss tangent (DMA) as a function of aging time and temperature. A model of yield stress versus crazing stress was proposed in this work to explain the ductile to brittle transition in fracture mode upon aging. Allen also noted a sharp increase in the rate of physical aging in polycarbonate above 80 C.

Petrie and Flick and Petrie^{40,42,61} have studied physical aging in terms of enthalpy and corresponding volume recovery. In Petrie's initial work, the changes in thermodynamic properties as a function of aging time were monitored using differential scanning calorimetry (DSC). The basis of this work was that the energy absorbed at the glass transition temperature, i.e., the area under the endothermic peak, can be related to the amount of enthalpy relaxation that occurred during aging. Comparison of enthalpy relaxation data to volume relaxation data showed an unexpected inconsistency in that the time scale for enthalpy relaxation was much longer than deduced from volume relaxation data.⁴² In their later work, results from dynamic mechanical analysis (DMA) spectra showed that the changes in modulus paralleled the extent of enthalpy relaxation that occurred during aging. From the results of this work it was concluded that the property changes inherent to physical aging were not related to the formation of structures involved in the development of crystallinity. More detailed studies performed later by Flick and Petrie on polycarbonate confirmed previous assessments and concluded that the only structural changes manifested by the aging process were those attributable to densification as a result of normal liquid-like packing corresponding to the near equilibrium glassy state. This contention was partially supported by the fact that there was no evidence of crystal formation in the physically aged polymers as measurable by X-ray diffraction techniques. X-ray diffraction data confirming this observation have been reported by other authors as well.^{31,47}

Adam, et al.³² performed work similar to Petrie and Flick and also demonstrated a relationship between enthalpy relaxation as a result of physical aging and the resultant mechanical properties. In this work, a relationship was drawn between the magnitude of the thermal energy associated with the DSC peak, and the additional mechanical energy required to deform an aged polymer. Adam also proposed that the reduction of impact strength as a function of aging was due to plastic instability.

⁶⁰G. Allen, et al, *J. Mater. Sci.*, 8, p. 1449, 1973.

⁶¹J. Flick and S. Petrie, Studies in Physical and Theoretical Chemistry, vol 10, A.G. Walton, ed., Elsevier, New York, p. 145, 1980.

Bauwens-Crowett and Bauwens³⁸ measured tensile yield stress of polycarbonate as a function of aging time and aging temperature. The data were related to the magnitude of the endothermic peak at the glass transition temperature from DSC scans of samples aged similarly. Based on their results they concluded that the change in yield stress must be associated with the enthalpy change that is found between the initial state of the polymer and the aged condition. They also proposed that yielding and annealing may be described by the same processes. An attempt to extend this concept to the formation of free volume and densification was taken up in later work,¹⁵ with the results indicating that the kinetics of annealing, yielding, and enthalpy relaxation are identical, but differ from those associated with free volume formation or densification during physical aging.

The work of Bauwens confirmed earlier observations by Washer in which isothermal contraction experiments on polycarbonate showed no correlation to enthalpy relaxation.⁶² Washer also demonstrated that WLF theory could not be satisfactorily applied to free volume relaxation after aging. A major conclusion drawn by Washer was that although enthalpy and mechanical properties are affected by annealing below the glass transition temperature, these changes could not be linked to a decrease in free volume because the decrease in free volume was too low to justify these changes.

Golden, et al.³³ proposed that the changes that resulted as a function of physical aging could be attributed to rearrangement into more ordered regions in the amorphous polymer. Golden's work included a study of the rate of change in various physical and mechanical properties of polycarbonate brought about by annealing at temperatures below the glass transition temperature. Results from mechanical testing and DMA were consistent with a stiffening of the material due to internal rearrangement and supported the idea of structural changes in the amorphous regions of the polymer bringing about an increase in order.

Bubeck and Bales^{50,55} extended the arguments that physical aging was a structural phenomenon that could not be totally explained in terms of free volume relaxation. This assessment was a result of extensive experimentation on several polymers, including polycarbonate. In their earlier work mechanical testing as a function of time at a given aging temperature mapped the ductile to brittle transition for the various polymers tested.⁵⁰ In addition, their work demonstrated that the coefficient of internal friction for polycarbonate would double after eight days of aging at 120 C. The post-yield-stress-drop was also shown to increase as a function of aging in agreement with Haward et al.⁵⁶ DMA

⁶²M. Washer, *Polym.*, 26, p. 1546, 1985.

was used as a means of assessing the conformational changes of the polymer molecules. Results indicated that in the region of the highest secondary transition in polycarbonate (80 C), the loss tangent ($\tan \delta$) decreases as a function of aging time at 120 C. This work was later supplemented by more extensive spectroscopic examination techniques including solid state variable temperature nuclear magnetic resonance (VTNMR) and Fourier transform infrared measurements (FTIR).⁵⁵ Bubeck and Bales determined that the ductile to brittle transition upon aging polycarbonate, and most glassy polymers, could not be attributed solely to densification (decrease in free volume), but may be attributed to molecular chain conformation effects as predicated by molecular structure. Morgan and O'Neal proposed that the conformational changes taking place are those leading to poorly packed parallel chain segments.⁶³

It is evident from the literature that the role of free volume in physical aging is not well understood. While Struik has shown how the changes in physical and mechanical properties can be explained in terms of changes in free volume, his work does not present any hard evidence that these changes are manifested as a result of the changes in free volume that occur with physical aging. Struik's work only shows that these changes parallel each other and act respective to one another in light of traditional free volume theory. Inconsistencies pointed out by other authors have led to skepticism that a free volume mechanism can be employed to describe the process of physical aging. In summary, Flick and Petrie have shown that the time scale for enthalpy relaxation is much greater than the time scale for free volume relaxation; Bauwens-Crowett and Bauwens concluded that the kinetics of annealing, yielding, and enthalpy relaxation were the same, but these differed from the kinetics associated with the free volume formation and densification; and Washer showed enthalpy and mechanical properties to be affected by aging, but the corresponding change in free volume was too low to justify these changes. The inconsistencies of the free volume argument may shift the emphasis of the mechanism responsible for physical aging to arguments involving conformational changes and structural rearrangement that have been proposed by Golden, Bubeck and Bales, Adam, et al., and Haward.

As proposed by Tant and Wilkes,³⁷ the problem discerning the role of free volume in the physical aging process lies in the ability to measure the actual distribution and amount of free volume present. Positron annihilation lifetime spectroscopy has been proven effective in characterizing

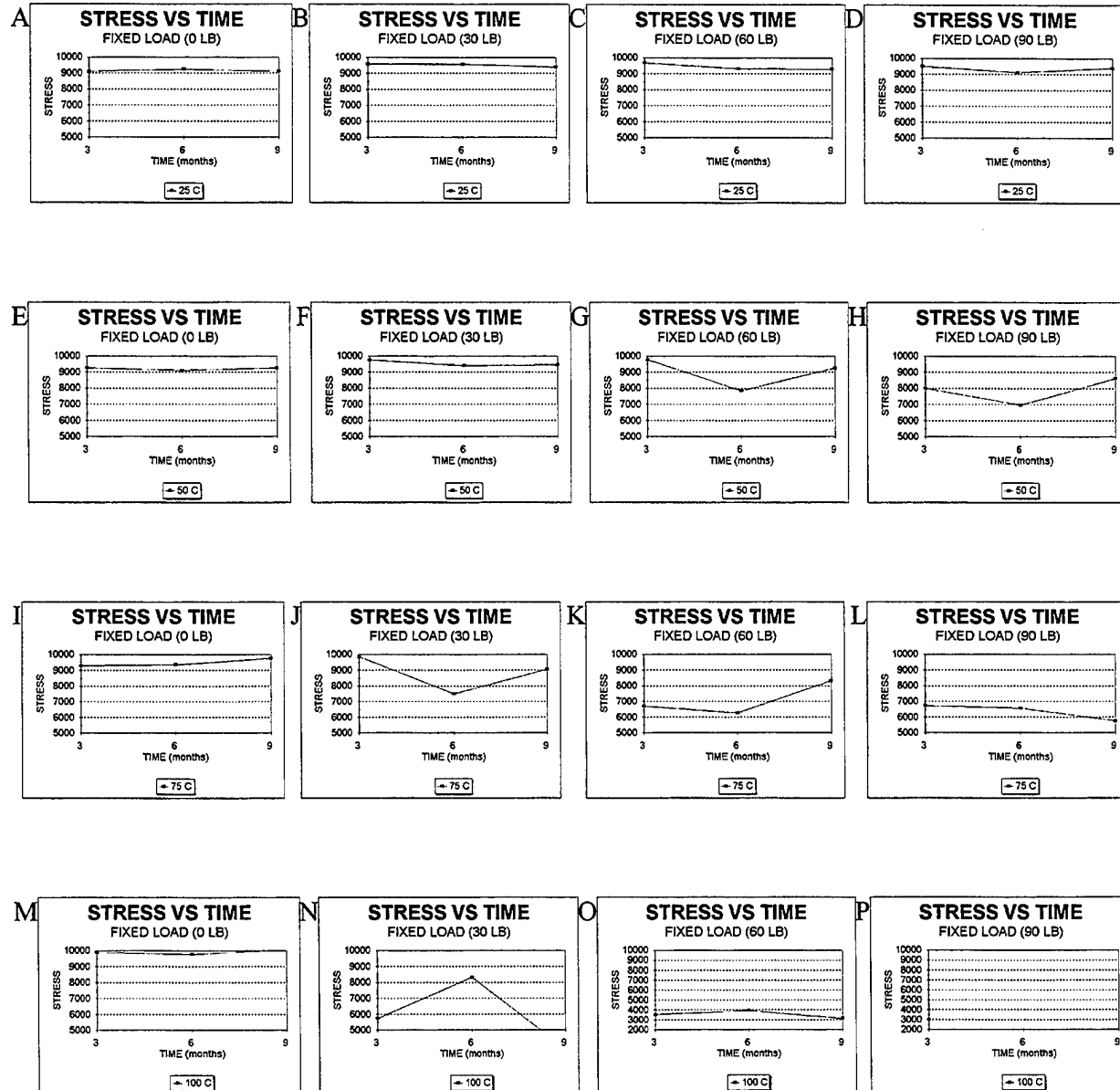
⁶³R. Morgan and J. O'Neal, *ACS Org. Coat. Plast. Prep.*, 34, p. 195, 1974.

both of these parameters in polymers. Thus, the premise for the use of PAS techniques in the work pursued under this contract.

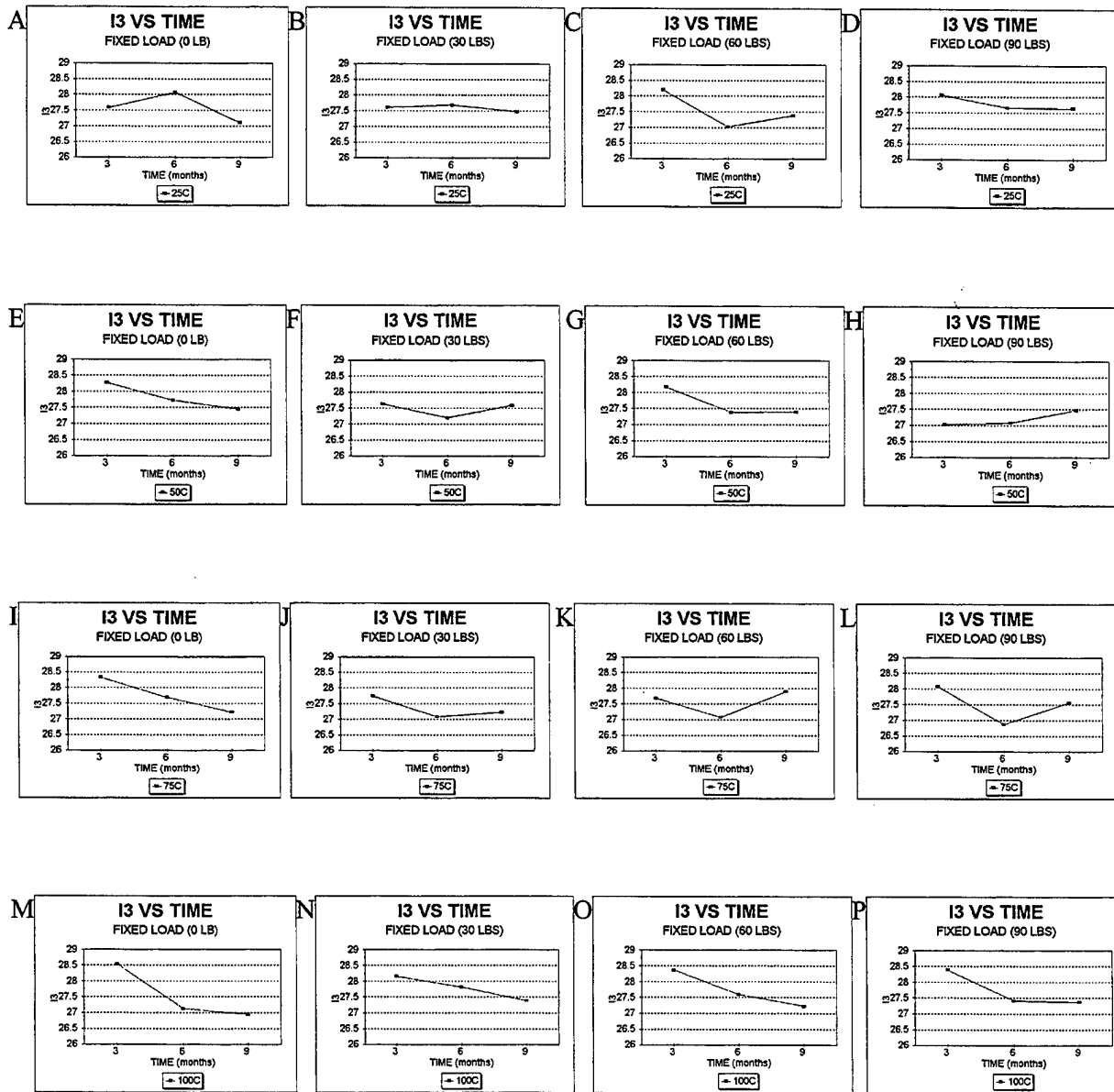
7. RESULTS AND DISCUSSION

The results of the testing program are presented in this section. Discussions will concern only the thin samples as the thick samples saw only temperature and provided no additional insight. Data are primarily presented through two sets of graphs. The first set of graphs (Graphs 1A thru 1P) demonstrates the changes in tensile stress properties as a function of time, temperature, and stress. The second set of graphs (Graphs 2A thru 2P) shows the changes in the number of free volume sites (%I-3) as measured by PALS. Test specimens were standard ASTM Type II tensile bars, with a load bearing area in the gage length measuring approximately 0.25 x 0.125 inches or 0.03125 in². All data were collected after test exposure periods of 3, 6, and 9 months. Test conditions included 0 (no load), 30, 60, and 90 lb. loading. Assuming purely elastic deformations in this range (i.e., no reduction in cross-sectional area), this corresponds to constant stress exposure conditions of 0, 960, 1920, 2880 psi, respectively, well below polycarbonate's yield stress of approximately 9000 to 9500 psi. Constant stress experiments were performed at temperatures of 25, 50, 75, and 100 C. Samples under the higher loads and higher temperature conditions such as P (100C and 90 lbs) often broke during exposure thus resulting in few or no stress vs. time data points

GRAPHS 1A- THRU 1P: Stress vs. Time



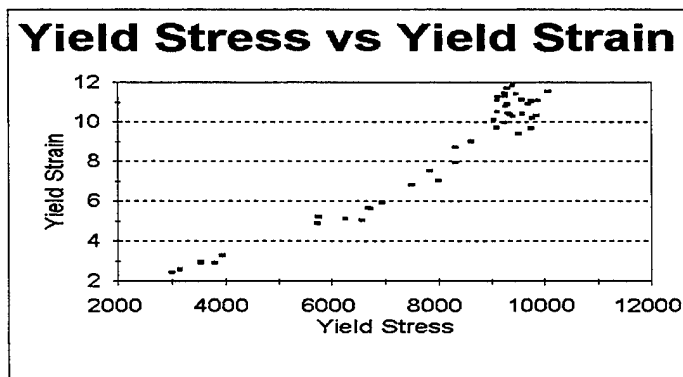
GRAPHS 2A THRU 2P:



7.1 Tensile Strength vs. Tensile Strain

There were measurable reductions in tensile stress and strain values due to the effects of exposure. However, the strain and stress responses were very similar in form. This is shown in the linear relationship of the plot of Yield Stress versus Yield Strain (Graph 3). There does not appear to be any relevant information found in the strain response that is not also seen in the stress response. Therefore, the remaining comparisons will focus on the stress response to minimize redundancy. The stress response was selected because it has a lower relative percentage of standard error than the strain response.

Graph 3: Tensile Stress vs. Tensile Yield



7.2 Tensile Strength Data - Results

The tensile strength data demonstrated some interesting changes as a function of exposure time, temperature and loading. While some of these changes are subtle, they are important and should be noted and discussed in terms of the processes that may be accounting for these changes. The tensile strength data are best presented as a function of the constant loading conditions during aging and then

discussed in terms of changes that are occurring as a function of aging time and temperature. It will be noted that within and among these data sets, certain changes can be noted to occur as a function of aging time. The evolution of these changes is significant.

- (1) **0 lb. Loading** - There is a slight increase in the yield strength for all of the samples relative to the 25 C samples, with a notable increase in yield strength in all the samples aged at 100 C and the samples aged at 75 C for 9 months. The yield strength of the test specimens remains essentially constant as a function of aging time for the 25 and 50 C samples.
- (2) **30 lb. Loading** - The 30-lb. loading data demonstrated a slight increase in tensile strength relative to the 0-lb. load data at all temperatures except for the 100 C data, which showed a sharp decrease in yield strength after 3 months of aging. The 6-month and 9-month tensile data for the 100 C experiments were affected by stress cracking and premature failure. The 75 C tensile data showed a slight increase in tensile strength at the 3-month period, followed by a sharp decrease in tensile strength at 6 months, then a notable increase after 9-month data. The local minimum in this data provides the first evidence of the competing processes brought about as a consequence of the experimental design.
- (3) **60 lb. Loading** - The 60-lb. loading data is very similar to the 30-lb. loading data, but the tensile stress behavior is shifted to lower temperatures. Again, there is a slight increase in tensile strength at 25 C, but with some evidence of a slight decrease starting to occur in the 6- and 9-month data. The 50 C data shows a slight increase in tensile strength at 3 months, followed by a drop in strength at 6 months before increasing to a strength characteristic of the control samples after 9 months. The 75 C data also shows a local minimum, however, the yield strength at 3 months is significantly lower than the control sample values. Larger decreases are noted in the 100 C data, but this data was also affected by sample stress cracking.
- (4) **90 lb. Loading** - The 25 C 3-month data showed a slight increase in tensile strength relative to the control data, with a slight inflection in the data at 6 months at a value similar to the control samples, followed by a slight increase at 9 months. The 50 C data showed a very definite local minimum at 6 months. The 50 C 3-month data was markedly lower than the control data. The 9-month data appeared to be approaching the tensile strength values of the unaged samples. The 75 C data demonstrated very definite decreases at 3, 6, and 9 months. However, the 9-month data was affected by sample stress cracking. The 100 C data was severely affected by stress cracking, but it appears that the tensile properties of the samples were severely diminished (decreased) at these exposure conditions.

7.3 Tensile Strength Data - Discussion

The inflections or local minima demonstrated in the tensile strength data are obvious indicators of competing mechanisms fighting to control the tensile strength behavior. On one hand, there are mechanisms that are leading to an increase in tensile strength. On the other, there are mechanisms leading to a decrease in tensile properties. Furthermore, it is obvious that one or both of these mechanisms are a function of applied stress and/or temperature. It is unclear from the data what the mechanisms are, but they do not appear to be driven by free volume which does not consistently follow the same trends.

7.3.1. Increase in Tensile Strength. The increase in tensile strength is a direct result of the classical *physical aging* process that occurs in amorphous polymeric materials as brought about by the non-equilibrium nature of these materials. It is this process that the current program was designed to investigate. The physical aging process in amorphous polymers has already been discussed in detail in the opening sections of this report. As such, only the characteristics of the data sets that demonstrate that the physical aging process is occurring will be discussed in this section.

As previously discussed, physical aging in amorphous polymers can be characterized by an increase in tensile yield strength as a function of aging time (t_a) and aging temperature (T_a). In the absence of external influences, the effects of physical aging (e.g. increase in tensile strength) increase as a function of aging time at a given aging temperature. Furthermore, at a given aging time the effects of physical aging will be more prevalent in samples aged closer to T_g (the glass transition temperature of the polymer). This behavior is exhibited in the tensile data reported here. At zero load and constant aging time, there is a trend in the data for the tensile yield stress of the samples to increase as a function of aging temperature. For instance, the yield stress of the 25 C samples is approximately 9,000 psi for all aging times, compared to the yield stress of the 100 C samples which is consistently about 10,000 psi.

It is also significant to note that the data at 25 C and 50 C remain relatively constant as a function of aging time, while the data at 75 C shows a slight increase in tensile strength after 6 months of aging. The transition in tensile strength behavior at 75 C is significant, as polycarbonate exhibits a β transition temperature in this range that is attributed to the onset of main chain molecular mobility. Thus, while physical aging does occur at temperatures below the β transition temperature of

polycarbonate, the rate of physical aging above the β transition is significantly enhanced. An increased rate of physical aging above the β transition temperature in polycarbonate has been noted by other authors, so the behavior noted in the data presented here might be expected.⁵⁷ The aging rate at 100 C is clearly greater than that exhibited at the lower temperatures, as the 3-month samples aged at 100 C already exhibit a significant increase in strength relative to the 3-month samples aged at the lower temperatures. While there is a continued increase in tensile strength at longer aging times at 100 C, the relative rate of increase with time is not a very strong function of time. This behavior supports the hypothesis that the rate of physical aging is a stronger function of aging temperature (and specifically $T_g - T_a$) than aging time (t_a).

Similar aging effects are noted in the samples aged under constant stress levels. However, the aging behavior is much more complex in these systems. The most significant thing to note in this data is the increased rate of aging at low times and low temperatures relative to the samples aged under zero stress conditions. For example, the samples aged for 3 months at 50 C and 75 C demonstrate an increase in tensile yield strength of the same order achieved by the 100 C/0 lb. load samples in the same 3-month period. This behavior is expected based on other works reported in the literature on physical aging in which the rate of physical aging is shown to increase under the application of applied strain.^{27,64,65,66}

The increased rate of physical aging after deformation is attributed to the increase in the distribution of relaxation times brought about by an increase in the amount of available free volume. Another way to look at this may be an increase in the population of higher energy conformations which contribute to the ductile behavior of polycarbonate with the energy input required for this transformation being supplied by the mechanical straining of the sample. Regardless of the mechanism argued, the net result is an increase in the relaxation time of the system so the system will be in a state that will allow for an increased rate of physical aging. This behavior is consistent with the theory that the rate of physical aging is not only a function of temperature and time, but also a function of the departure of the system from its equilibrium structure. Thus, under strain, the system is drawn further from equilibrium and its

⁶⁴M. Litt and S. Torp, *J. Appl. Phys.*, 44 (10), p.42, 1973.

⁶⁵R. Pixa, et al., *Polym. Bull.*, 16, p. 381, 1986.

⁶⁶J. Bartos, et al., *Polym.*, 31, p. 1678, 1990

initial rate of relaxation toward equilibrium is enhanced by the increased number of molecular processes available to participate in the subsequent relaxation toward equilibrium.

The fact that the rate of physical aging increases under induced strains was used in the initial design of the experiments conducted under this program, setting the foundation for the hypothesis that the rate of physical aging would be increased under applied loads at the given aging temperatures. However, one key factor was neglected in the design of the initial experiments: all of the works that demonstrate an increased rate of physical aging after deformation used experiments that were performed either at constant strain (where stress relaxation can occur), or the loads that were applied to the sample were removed prior to measuring the rate of physical aging. Under both of these circumstances, the polymer system is initially displaced from its initial *quasi-equilibrium* condition to a state further away from its equilibrium structure, and then allowed to relax freely back toward its equilibrium structure. The greater the displacement (up to the elastic limit) the faster the relaxation back toward equilibrium. Larger deformations have actually been shown to *de-age* physically aged amorphous samples, with some authors using a combined treatment of compression and high temperature annealing to completely erase all previous aging effects prior to the onset of their experiments.⁶⁷

The key difference in the current experiments is the fact that the load is applied during the entire course of the sample exposure period (constant stress). As a consequence, the samples are no longer able to relax back toward their equilibrium structure at an appreciable rate, because this relaxation process (physical aging) now has to compete with the molecular (structural) rearrangements taking place to reorient the molecules in a manner that allows them to support the applied load. Thus, in effect, the continued application of the applied load creates a competing process for physical aging.

7.3.2 Decrease in Tensile Strength. Structural and free volume arguments have been provided to explain the physical aging process in amorphous polymer systems. These same arguments can be used to explain the decrease in tensile yield strength in samples that have been subjected to external loads prior to testing. In the free volume argument, it is assumed that polymer yield is dictated by the available free volume. When a sufficient amount of free volume has been generated to allow the

⁶⁷C. Bauwens-Crowet and J. Bauwens, *Polym.*, 28, p. 1863, 1987.

molecular reorientation processes that constitute yielding to occur, then yielding will take place. Thus, when a polymer is pre-loaded and excess free volume is generated, and the polymer is then tested in tension before it is allowed to relax back to its equilibrium state, the amount of energy (stress) that needs to be applied to the polymer system to raise it to the critical level of free volume required for yield is now decreased since the polymer system was at an enhanced level of free volume at the start of the test. Therefore, polymers that have been pre-strained, or otherwise treated to increase their level of available free volume (e.g. fast quenching, swelling) will exhibit a decrease in yield strength in proportion to the magnitude of the excess available free volume. This same argument explains why polymers that are slow cooled or allowed to physically age for long periods of time before testing (while free volume relaxation occurs) demonstrate higher tensile yield strengths.

Structural arguments for the same phenomenon can be provided in terms of the relative populations of low (*trans*) and high (*cis*) energy conformations present in an amorphous polymer system at the time of testing. In the introductory sections, the structural conformations of polycarbonate were presented as well as a model explaining ductility and physical aging in polycarbonate in terms of these structural conformations. In the as-annealed state, the ductile behavior of polycarbonate was attributed to a sufficient population of high energy *trans-cis* conformations and enough available free volume for energy dissipation to occur via the crankshaft motion proposed by Jones. However, in the absence of external influences, the natural tendency is for the structure to be driven from the high energy *trans-cis* state to the lower energy *trans-trans* conformational state, which exhibits more order and better structural packing. Thus, as a function of time, the population of *trans-cis* conformations will decrease as the population of *trans-trans* conformations increases. This process not only inhibits molecular mobility by decreasing the population of high energy states than can absorb energy by transitioning to a lower energy state, but is also has a net negative effect on the available free volume that allowed this process to occur in the first place. This combination of events is used to explain the ductile to brittle transition exhibited by many amorphous polymers as a function of aging time or low temperature exposure, as well as many aspects of the *physical aging* phenomenon, including an increase in tensile yield properties as a function of aging time and aging temperature.

The decrease in tensile yield properties under loads can also be explained in terms of these arguments. Robertson⁶⁸ provides an excellent review of this process in terms of Eyring's model of

⁶⁸R. Robertson, *J. Chem. Phys.*, 44 (10), p. 3950, 1966.

yielding in polymeric materials. In his work, Robertson demonstrated it was possible to increase the population of high energy conformations by the application of stress, thus driving the system further from equilibrium structure and packing. Since the higher energy or *flexed* bonds exhibit a higher degree of mobility and freer rotation about the bonds in the polymer backbone, then the net effect of increasing the population of these conformations is a resultant decrease in the rigidity of the polymer system. In the current system, the decrease in rigidity is reflected as an overall decrease in the yield strength of the polycarbonate samples aged under load. The decrease in yield strength can also be explained in terms of the relative population of low vs. high energy conformations and assuming that a specific number of high energy conformations must be available for yielding to occur. Since pre-stressing causes a shift in the distribution of conformations toward higher energy, if the system is tested before the structure can relax back toward equilibrium, fewer segments need to be converted from the low to the high energy state for yielding to occur, so energy input requirements are lower. The net result is a decrease in the tensile yield strength of polymers tested shortly after being subjected to external stresses.

7.3.3. Competing Processes. The process of physical aging has been presented as an overall decrease in the available free volume in a polymeric system, or a net decrease in the population of high energy conformations responsible for polymer ductility as the amorphous structure relaxes toward its lower energy equilibrium structure and packing density. The decrease in tensile yield properties has been attributed to an increase in available free volume and high energy conformations brought about by the application of external loads. This behavior is best described as a *strain softening* phenomenon. It is obvious, that the effects of physical aging and strain softening are competing during the course of this program and these competing forces account for the inflection points noted in the tensile strength data.

In the absence of external stress, tensile strength was shown to increase through conventional physical aging arguments. At low temperature and stress levels, and short aging times, the rate of physical aging was actually enhanced by the increase in molecular mobility brought about by the applied loads. However, at short to moderate aging times, the rate of strain softening is significantly faster than the rate of physical aging and a stronger function of temperature and loading. If the applied stress had been removed after its initial application, the increase in temperature would have driven the system toward its lower energy equilibrium structure (physical aging) at a much faster rate than the samples aged without the application of stress (the rate of physical aging increasing in proportion to the applied load, or the initial displacement of the system from equilibrium.). However, since the loads were not removed during the aging process, the external stress continued to drive the system further from

equilibrium at a rate proportional to the increase in temperature and loading. The increase in the rate of strain softening being expected at higher temperatures and higher loads as molecular mobility and polymer flow are enhanced.

The existence of the inflections points in the data indicate that at some point the rate of physical aging increases to a point where it is able to overcome the rate of strain softening, after which the tensile yield properties of the system begin to increase as the structure regains its rigidity through the physical aging process. In the absence of non-competing effects and assuming sufficient loading conditions, the rate of strain softening is expected to proceed fairly rapidly relative to the rate of physical aging. However, since the stress level is constant, the rate of strain softening is expected to decrease as the molecules in the system are able to reorient themselves in a manner sufficient to sustain the external load. The rate of strain softening is further decreased by the increase in the rigidity of the system as a consequence of the combined effects of physical aging. All other variables being constant, the rate of physical aging has been shown to increase in proportion to the departure of the system from equilibrium. While small, the effects of physical aging are noted in the short term aging data under no loads and higher temperatures. Under the application of applied stress, the rate of physical aging is shown to be enhanced initially, but is quickly overtaken by the rate of strain softening. However, while the rate of strain softening decreases as a function of time under a constant load, the rate of physical aging is only further enhanced by any subsequent departures of the system from its equilibrium structure. As a consequence, the rate of physical aging is eventually accelerated toward equilibrium as the strain softening effects are diminished. The net result is a local minimum in the tensile yield strength, followed by an accelerated rate of physical aging (and increase in tensile yield strength) after the strain softening effects have been minimized.

7.4 PALS Data - Results

PALS data were collected on the ASTM tensile bars after exposure. Tensile bars were cut in half and the two pieces were placed in a sample holder on either side of the positron source for data collection. All PALS data were collected in the gage of the tensile specimens. Some deviations in the PALS data may be attributed to asymmetric sample loading conditions. Other deviations may be attributed to the dynamic nature of the samples under investigation. This factor can be significant and is discussed subsequently.

The PALS data is presented as a function of constant loading conditions during aging and discussed in terms of changes that are occurring as a function of aging time and temperature. Like the tensile strength data, the PALS data demonstrated some interesting changes as a function of exposure and exposure conditions. Some of these changes can be directly correlated to the physical processes competing during the aging experiments. However, there are a number of changes that cannot, most likely due to the dynamic nature of the systems that were being interrogated.

- (1) **0 lb. Loading** - The zero-loading data demonstrated some peculiar behavior at 25 C, with a maximum in the data exhibited at 6 months. This effect is believed to be anomalous. A general trend for a decrease in %I-3 as a function of aging time is demonstrated between the 3-month and 9-month data. The 50 C, 75 C, and 100 C data all show more classical changes in free volume as a function of aging time and aging temperature, with larger decreases in %I-3 noted at higher aging temperatures for similar aging times.
- (2) **30 lb. Loading** - The 30-lb. load data showed no changes at 25 C. The 50 C, 75 C, and 100 C data all showed lower %I-3 values after 3 months of aging relative to the 0 lb. loading samples, while the 9-month values tended to be higher than the 0 lb. sample data. Inflection points were noted at 6 months in the 50 C and 75 C data.
- (3) **60 lb. Loading** - The 60-lb. loading data showed clear inflection points at 6 months even at 25 C, but the overall trend in the data as it progressed to 9 months was unclear.
- (4) **90 lb. Loading** - Inflections points were also noted in the 90 lb. loading data, but again the overall direction of the data was unclear.

7.5 PALS Data - Discussion

The PALS data were disappointing as there was too much scatter in the data to depict any real trends or to draw any strong correlations with the tensile stress data. Two factors contributed to the outcome of the PALS investigation: (1) the existence of the competing processes between physical aging and strain softening effects; and (2) the fact most samples were probably not in their equilibrium free volume state at the time of the PALS measurements (dynamic system effects). A third factor, related to the validity of the free volume argument for explaining the physical properties of polymer systems, and specifically the process of physical aging, has already been addressed in the introductory sections of this report. One of the factors contributing to the lack of correlation among the PALS data could be the inability of the free volume argument to adequately address the changes in physical properties that occur during physical aging.

7.5.1 Competing Processes. The factors that were competing during the course of the exposure experiments have already been discussed in detail in the previous section. Free volume arguments were presented for each of these processes to explain their effects on the tensile properties of the polycarbonate samples. Some of these arguments will be expanded upon here to demonstrate the complexity of the free volume environment during the exposure experiments.

According to the free volume argument for physical aging, in the absence of external loading conditions, the free volume of an amorphous system is expected to decrease as a function of time at a rate that is inversely proportional to the temperature at which the aging process is occurring. The magnitude of the free volume decrease is proportional to the difference between the aging temperature and the glass transition temperature of the polymer system. For the most part, the free volume data collected at zero loading reflected this behavior, although it is doubtful the systems tested were truly in equilibrium with respect to their free volume state at the time of testing.

The samples tested under load exhibited a different behavior. The free volume state in these samples is a complex function of free volume dilation due to stress (increase in free volume), a redistribution of free volume and possibly a slight decrease in free volume as a result of local molecular reorientations taking place to counteract the effects of external loading, and a decrease in free volume as a result of physical aging. The tensile strength data provided clear evidence of the competing factors associated with external loading (strain softening) and the rate of physical aging. For the samples exposed at higher temperature, the free volume behavior is further complicated by an increase in free volume as a consequence of thermal expansion, particularly for the samples aged at 100 C as a very definite increase in free volume is expected with the onset of local main chain molecular motion as these samples are heated through the β transition temperature region.

In-situ PALS measurements taken on the test samples would have provided a clear indication of the dynamic free volume effects taking place in these samples under the complex experimental conditions, providing a clear means of determining which effects are dominating the behavior of the amorphous polymer system. *In-situ* PALS measurements would also make it possible to follow the changes in free volume that occur when the external loads are removed and the samples are cooled to room temperature for testing. However, the time scale of the free volume relaxation process toward its equilibrium room temperature value is extremely long making it almost impossible to characterize the equilibrium free volume state that uniquely characterizes the properties of an amorphous polymer system in a reasonable experimental time frame. Thus, the dynamic effects noted in the PALS data become extremely important in a study such as the one performed under this contract.

7.5.2 Explanation of Dynamic Effects in PALS Data. After the initial annealing, all of the samples were exposed for set periods of time, under load and at temperature. The samples were then removed from their test fixtures and stored at room temperature prior to testing. Since there were a large number of samples, the PALS measurements on each sample set required a finite period of time. *During this time, relaxation processes were occurring.* These processes consisted of free volume relaxations occurring as a result of changes in temperature and changes in loading conditions. The free volume changes associated with removing the samples from their higher temperature environments have been characterized *in-situ* by PALS in other investigations.⁶⁹ These measurements have shown τ_3 to instantaneously decrease to its low temperature value (the temperature of the experiments), while %I-3 showed a gradual relaxation as a function of time. Relaxation times for %I-3 of the order of weeks are not uncommon for samples cooled to room temperature from higher temperatures. The rate of %I-3 relaxation is a function of aging temperature and cooling rate. While not as dramatic, similar %I-3/ τ_3 behavior have been demonstrated for samples which were stressed at room temperature and then allowed to relax after the removal of the stress while PALS spectra were collected continuously.⁷⁰ While there are no known studies of free volume relaxation (as measured by PALS) after combined exposure to high temperatures and loading, one might expect that the rate of the free volume (%I-3) relaxation process at room temperature and zero load would be accelerated as a result of the factors previously discussed regarding the accelerated rates of physical aging after external loading.

The main problem with the issues raised by the previous discussion, is that it is difficult to determine when the PALS measurements should be taken. To glean any relationship between free volume and any properties of a given system, the PALS measurements must be performed when the system is in *equilibrium* or at some point during the relaxation process that can be normalized out of the data. Due to the number of samples, it is impossible to take all of the PALS measurements immediately after the exposure experiments are terminated. Furthermore, this would not make sense as the free volume (%I-3) state of these systems would be undergoing rapid changes during the course of the PALS experiments. Even if this were not the case, it would have been time intensive and cost prohibitive to create an exposure and testing schedule to accommodate immediate PALS measurements. Ideally, PALS measurements would be taken once the individual samples have reached their *equilibrium* free volume

⁶⁹K. J. Heater and P. L. Jones, *Proceedings, Materials Research Society*, 215, p 207, 1990.

⁷⁰M.Y. Ruan, et al., *Materials Science Forum*, 105-110, p. 1691, 1992.

state at a given test temperature, neglecting the slow relaxation process that might be occurring as a result of continued physical aging at the temperature of the PALS experiment. At lower temperatures, this might be a plausible alternative, since the time scale for the physical aging process would be extremely long relative to the relaxation processes occurring as a result of temperature quenching or stress relaxation. However, the question then becomes how long does it take for the systems to reach their *equilibrium* free volume state? Some estimates can be made experimentally, but time frames of the order of weeks or months are likely for the best results. Unfortunately, in the end, the issues of experimental design become an issue of time and money. Data are collected as efficiently as possible, and one hopes the effects of the experimental variables far outweigh those of the non-experimental variables.

The dynamic effects of the free volume relaxation processes going on after the samples have been aged and during the course of the fairly random PALS experiments is believed to have strongly affected the results of the PALS investigation, essentially overshadowing any correlations that might be drawn between the equilibrium free volume data and the tensile test data. However, given the fact that the experimental design resulted in generating two opposing effects in the majority of the samples under investigation, it is highly unlikely that the results of the program would have been favorable anyway, even if equilibrium free volume data were available. The basis for this statement revolves around the fact that the competing processes were driving the free volume state and the physical properties of the polycarbonate samples in different directions characterized by different failure modes. As a consequence, the ability to create a *master curve* which characterized the rate of physical aging in polycarbonate was severely limited by the initial assumptions used in the design of the proposed experiments.

7.5.3 Validity of the Free Volume Argument. A third factor to examine is the actual validity of the free volume argument, and therefore the foundation on which the hypothesis of the current program is based. Many authors have questioned the validity of this argument and have offered alternative arguments to explain the process of physical aging. The most prominent of these arguments is the model based on structural or conformational changes occurring in the polymer system as a function of physical aging.

The free volume argument of physical aging gained popularity as a result of specific volume measurements performed on physically aged amorphous polymer samples. These measurements demonstrated a decrease in specific volume as a consequence of physical aging as a consequence of

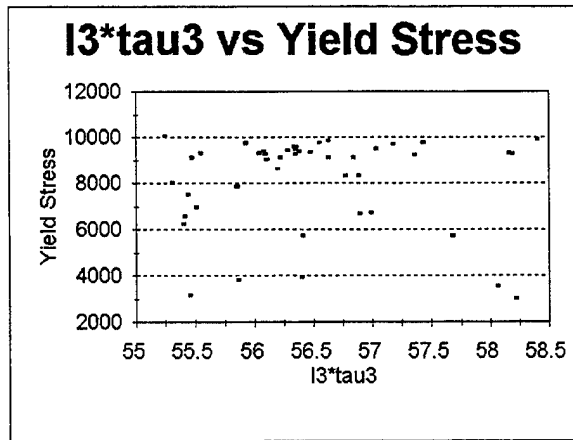
sample densification brought about by an increase in packing density of the molecular chains as they relaxed toward their equilibrium structure. This densification process was presumed to occur as a direct consequence of a decrease in free volume during the physical aging process. Further proliferating the free volume argument was the fact that the changes in the mechanical properties of physically aged amorphous systems could be readily explained in terms of free volume arguments. For example the increase in tensile yield strength as a consequence of physical aging could easily be explained as an increase in the rigidity of a polymer system brought about by a reduction in free volume. Thus, the primary question is, *can free volume arguments really be used to explain the changes in mechanical properties that occur during physical aging?*

Many authors certainly feel that the answer to this question is *no* and have offered alternative arguments to explain the process of physical aging in amorphous polymer systems. The most prominent argument would indicate that the effects of physical aging are a consequence of structural changes occurring in the polymer system that result in a shift in the population of conformational states from a higher energy conformational state to a lower energy conformational state. The change in conformations then allows for a more efficient level of molecular packing that is eventually reflected by an increase in density and a decrease in available free volume. However, the time scale of the free volume changes is slow compared to the time scale of the processes that account for the effects of physical aging in amorphous polymer systems. Thus, while a decrease in free volume may be a consequence of the physical aging process, these changes are not likely to be responsible for the changes in polymer properties noted as a consequence of physical aging.

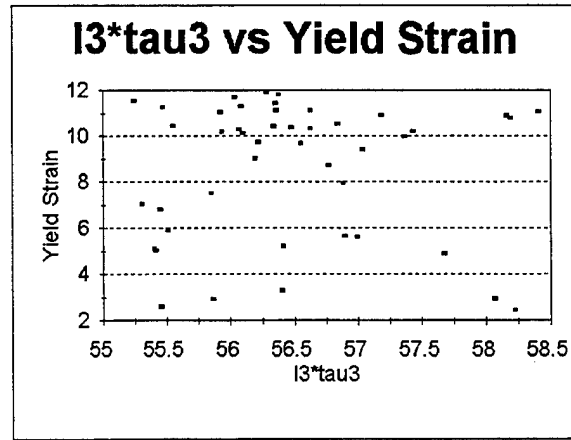
8. SUMMARY

The primary issue that was investigated in this program was the relationship between physically induced *aging* and free volume changes. It was determined that tensile properties do not change as a result of changes in free volume, as dramatic tensile changes were noticed without measurable changes in free volume. This is best seen by the wide range of tensile values show in Graphs 4, 5. Graph 4 is a plot of all of the data associated with FVM ($I_3 \cdot \tau^3$) vs. Yield Stress. Graph 5 is a plot of the FVM ($I_3 \cdot \tau^3$) vs. Yield Strain data.

Graph 4: FVM ($I3 \cdot \tau3$) vs. Yield Stress

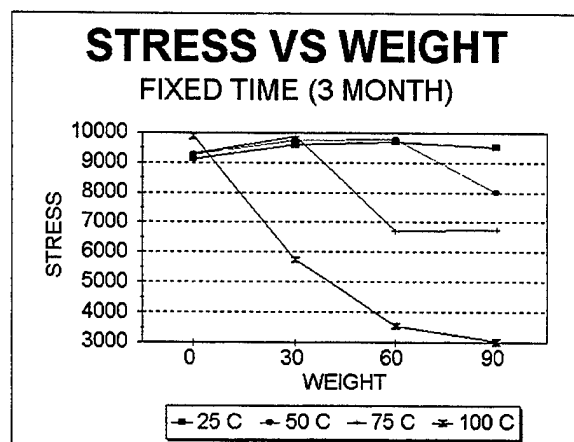


Graph 5: FVM ($I3 \cdot \tau3$) vs. Yield Strain

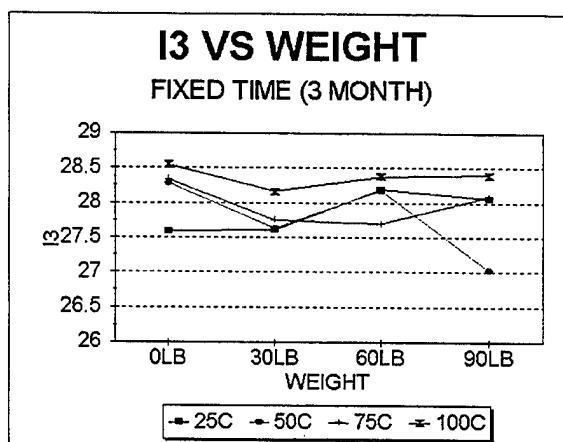


There were no measurable changes in free volume in either $\tau3$ or $I3$ while there were several samples that were exposed to high temperature and high loads that had dramatic reductions in yield strength and yield strain values. (See graphs 6 and 7). All combinations of $I3$, $\tau3$, yield stress and yield strain were compared and there was no additional correlation information to be found from these combinations when considering all of the exposure conditions.

Graph 6: Yield Stress vs. Weight (@ 3 months)



Graph 7: I3 vs. Weight (@ 3 months)



Unfortunately, while there are trends due to the influences of time, temperature and loads, there does not appear to be any detectable relationship between free volume and the physical response to the tested exposures as seen in the Yield Stress and Yield Strain values and the I3 and τ_3 components.

9. CONCLUSIONS

The initial hypothesis on which the current program was designed appears not to be supported by the data. As a result, the design of the program leads to the creation of two effects that were competing with each other for dominance over the course of the experimental time frame. The effect of temperature exposure over time was to harden the material while the result of loading the samples under a constant stress over time was a softening of the samples. Furthermore, the ability to collect meaningful free volume data was most likely inhibited by dynamic changes in the free volume state of the samples being characterized by PALS. One major issue that was discussed in this report, but not directly substantiated by the generated data in this program, is the actual validity of the free volume argument for physical aging. While free volume arguments for physical aging are frequently presented in the literature on physical aging, there are just as many, if not more, authors who believe the process of physical aging cannot be accounted for in terms of free volume arguments alone. Thus, even after the experimental issues are addressed, the basic premise on which the current investigation was based needs to be thoroughly scrutinized before a similar task is proposed or pursued.

APPENDIX DATA FILES

Table A-1. I3 Results

Exposure Code	3-Month Avg.	3-Month Std.	6-Month Avg.	6-Month Std.	9-Month Avg.	9-Month Std.
A (25 C, 0 Lb)	2.053	0.008	2.044	0.007	2.046	0.002
B (50 C, 0 Lb)	2.041	0.008	2.036	0.008	2.049	0.006
C (75 C, 0 Lb)	2.029	0.001	2.056	0.004	2.047	0.001
D (100 C, 0 Lb)	2.033	0.014	2.033	0.002	2.040	0.003
E (25 C, 30 Lb)	2.058	0.021	2.051	0.001	2.053	0.005
F (50 C, 30 Lb)	2.047	0.002	2.062	0.003	2.043	0.002
G (75 C, 30 Lb)	2.039	0.009	2.040	0.004	2.047	0.012
H (100 C, 30 Lb)	2.047	0.012	2.050	0.005	2.045	0.004
I (25 C, 60 Lb)	2.053	0.016	2.040	0.012	2.054	0.001
J (50 C, 60 Lb)	2.041	0.006	2.048	0.019	2.061	0.002
K (75 C, 60 Lb)	2.055	0.001	2.046	0.010	2.035	0.008
L (100 C, 60 Lb)	2.029	0.000	2.062	0.001	2.046	0.011
M (25 C, 90 Lb)	2.046	0.005	2.062	0.014	2.050	0.006
N (50 C, 90 Lb)	2.09	0.008	2.045	0.010	2.040	0.000
O (75 C, 90 Lb)	2.046	0.002	2.044	0.008	2.037	0.002
P (100 C, 90 Lb)	2.050	0.004	2.054	0.006	2.042	0.008

Table A-2. Stress Results

Exposure Code	3-Month Avg.	3-Month Std.	6-Month Avg.	6-Month Std.	9-Month Avg.	9-Month Std.
A (25 C, 0 Lb)	9114	18	9252	123	9123	98
B (50 C, 0 Lb)	9590	105	9580	253	9413	74
C (75 C, 0 Lb)	9697	214	9327	104	9302	73
D (100 C, 0 Lb)	9516	262	9105	202	9394	81
E (25 C, 30 Lb)	9271	228	9109	216	9262	181
F (50 C, 30 Lb)	9762	143	9411	63	9467	31
G (75 C, 30 Lb)	9784	94	7851	1932	9265	84
H (100 C, 30 Lb)	8003	877	6955	1569	8624	1057
I (25 C, 60 Lb)	9300	225	9357	131	9756	120
J (50 C, 60 Lb)	9859	161	7510	1923	9053	131
K (75 C, 60 Lb)	6699	1352	6263	748	8324	592
L (100 C, 60 Lb)	6736	1005	6574	654	5757	424
M (25 C, 90 Lb)	9888	206	9773	63	10075	121
N (50 C, 90 Lb)	5740	777	8325	1652	3807	1508
O (75 C, 90 Lb)	3550	384	3943	877	3165	375
P (100 C, 90 Lb)	3012	93				
Q(125C, 0 lb)						