

**EFFECT OF PHOTOAGEING AND PLASTICIZER CONTENT ON  
THE MECHANICAL AND ADHESIVE PROPERTIES OF  
POLYVINYLBUTYRAL**

by

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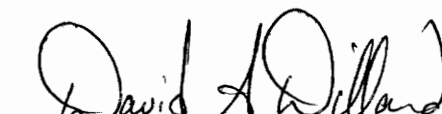
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MATERIALS SCIENCE AND ENGINEERING

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**ABSTRACT**

The objective of this study is to characterize the mechanical and adhesive properties of polyvinylbutyral and determine the effect of plasticizer content and photoageing on these properties. This data would be used to understand how the performance of laminated safety glass is related to the choice of adhesive interlayer.

Samples of PVB plasticized with 0 to 40% butyl benzyl phthalate by weight were analyzed using a single strain rate tensile test, dynamic mechanical thermal analysis and a 135° peel test. Two regimes of behavior were identified. PVB with low plasticizer contents, up to 10%, acts as a glassy polymer at room temperature. At higher plasticizer concentrations, greater than 20%, the material becomes elastomeric, with increased ductility and decreased moduli. The adhesive strength of each of the formulations was similar if compared at their respective glass transition temperatures. At room

temperature, the heavily plasticized formulations had good adhesive strength whereas the less plasticized formulations readily debonded from the glass. These results suggest that PVB plasticized with between 20 and 40% plasticizer content is highly suitable as an interlayer material.

UV radiation exposure was used to simulate the effect of sunlight on PVB. Forty micron thick samples were irradiated for up to 1000 hours of exposure time and analyzed using FTIR spectroscopy. It was determined that photodegradation had occurred in the form of a breakdown of the acetal ring structure in the vinyl butyral function.

Similar treatment of 0.75 mm thick samples produced no major degradation in the mechanical or adhesive properties of the material. This is an unexpected result that conflicts with the obvious degradation discovered during FTIR spectroscopic testing. This is most likely due to the increased thickness of the mechanical samples and corresponding lower UV dosage per polymer chain.

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# I. Introduction

The use of polyvinylbutyral (PVB) in laminated safety glass began in the mid-1930's. The properties of this new interlayer material led to significant improvement in the performance of the composite over the original laminates made with cellulose acetate or cellulose nitrate. To date, published research on this subject has concentrated on the performance of safety glass as a unit with little information given about the composition or properties of the interlayer material. The research described within attempts to shed further light on the properties of PVB and its interactions with sheet glass. The ultimate goal being to better understand and hopefully model laminated glass structures, both in their initial performance and after years of service.

Since the late 1980's there has been a resurgence of published research concerning laminated safety glass. Much of this work has centered around determining the effectiveness of laminated glass as an architectural glazing. The performance criteria for such glass are many and varied. They include pressure loading capability, impact resistance, long term durability, and for safety glazings - a safe failure mode. The ability of laminated glass to meet these criteria is strongly dependant on the properties of the individual layers and the interactions between these materials.

How the properties of sheet glass and the interlayer adhesive interact to form the unique properties of laminated safety glass is not yet well understood. Even less well understood is how the specific environmental conditions to which the composites are

subjected affect these interactions. Glass, being relatively inert, is not dramatically affected by temperature extremes, humidity, or UV radiation. The mechanical properties of PVB, like most hydrophilic polymers, are affected by extremes in temperature or humidity. PVB has been shown to degrade in the presence of UV radiation.<sup>35,36</sup> Therefore, the focus of this research effort is the interlayer, polyvinylbutyral.

In attempting to fully understand the polymer interlayer material it is important to first recognize the environment and loading conditions to which it will be subjected. Of primary importance in architectural applications, the adhesive interlayer must support at least some of the static load if the glass unit is set at any angle other than vertical. This includes the weight of the glass itself as well as any additional loadings such as snow. In such an application, the temperature of the glass and therefore the interlayer material may be below freezing during the winter and above 100°F in the summer. If properly sealed, the material should not be subjected to humidity changes during its service life.

Safety glass must also be resistant to impact. This resistance is a complicated function of the toughness of the glass, the energy absorbing characteristics of the interlayer and the adhesion between the layers. By separating the two layers of glass, PVB can prevent cracks forming in the outer layer from transferring to the second layer. Further, the polymer interlayer absorbs large amounts of energy during impact loading. This energy absorption characteristic is related to the high frequency, or dynamic loading properties of the polymer as well as the degree of adhesive bonding between the glass

and the interlayer.

This last property, adhesion, is also directly related to the ability of the composite to fail in a safe mode. Traditional single pane windows will shatter upon impact, even if the glass is tempered or heat treated. This shattering results in the emission of sharp glass shards as projectiles which have the potential to cause further damage. By adhering to the glass and resisting tear, PVB interlayers prevent the emission of the shards generated thus eliminating the possibility of projectile damage.

Finally, there is a side effect of using PVB as an interlayer in glass laminates. PVB absorbs UV light up to 400 nm, the beginning of the visible spectrum.<sup>34</sup> This is beneficial to the consumer and yet leads to chemical degradation of the polymer. It is beneficial to the user because damaging UV rays will be blocked, thus reducing carpet fading, possible eye damage and other negative effects of sunlight. Unfortunately, it has been shown that absorbed energy leads to photoinduced chemical degradation in PVB such as opening of the acetal ring structure in the backbone and crosslinking. Such dramatic changes in the structure of the polymer will alter the performance of the interlayer and change the properties of the composite.

How well safety glass meets these four major criteria for architectural glazings is directly related to the chemical, physical and adhesive characteristics of PVB. The research described herein will focus on these interlayer properties which include: static and dynamic mechanical properties, adhesion to glass and the effect of UV absorption on

all of the above.

## II. Literature Review

### 2.1 History and Uses

Polyvinylbutyral replaced cellulose acetate and cellulose nitrate as the adhesive interlayer in laminated safety glass (LSG) in the mid to late 1930's.<sup>1,2</sup> At this time, LSG was primarily used in automobile windshields. In this role, the primary objective of the interlayer is to prevent the generation of glass shard projectiles from the windshield during collision.

The use of a tough interlayer material also provides resistance to penetration of the glass by small objects such as road gravel.<sup>3</sup> Furthermore, the interlayer must be formulated in such a way as to minimize the damage to an occupant thrown into the windshield during an accident. This requires that the occupant be subjected to a minimum deceleration force and be retained within the vehicle. High elasticity and tear resistance become extremely important characteristics of the interlayer.

These same properties make LSG formulated with PVB a good candidate for aircraft windows. Such an application requires strict tailoring of the material to the application and numerous studies have been undertaken to determine the necessary properties and performance of LSG. Unfortunately for the research community, these studies use proprietary materials with the end result that no formulation information is normally given.<sup>4,5</sup>



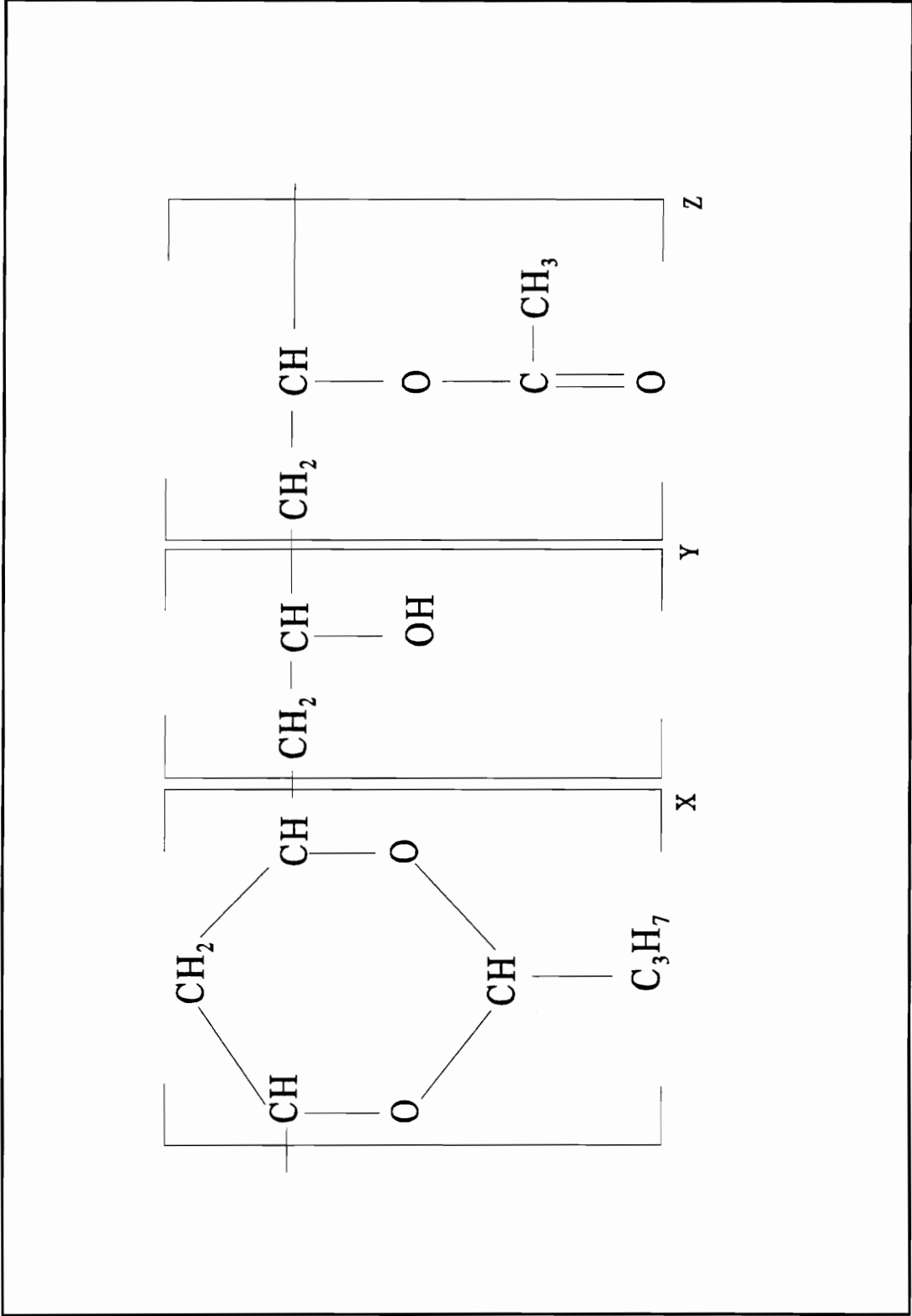
In the early 1970's laminated safety glass was introduced into the architectural marketplace. Most notable of these first structures was the glass construction in the Sydney Opera House.<sup>6</sup> The role of safety glass is different for architectural applications with the biggest change being the fact that the glass pane is now considered a load bearing structure. The purpose of the laminate changes from occupant retention to maintenance of structural integrity after glass fracture while maintaining its role of protection against object penetration. This new application generated interest in related research in the 1980's due to the need for a better understanding of laminate capabilities in light of hurricane damage in skyscrapers and other tall buildings.<sup>7</sup>

Today LSG with a plasticized PVB interlayer is used in a wide variety of applications including automotive windshields, architectural glass, airplane windscreens, railroad car windshields as well as test equipment and other applications where a degree of burst protection is required. These widely varied applications require a more detailed understanding of the properties of the composite with particular emphasis on interlayer characteristics.

## 2.2 Structure

PVB is a terpolymer formed by the reaction of butyraldehyde with Polyvinyl Alcohol (PVA). The reaction does not proceed to completion and 10-20% of unreacted PVA remains in the final structure (Figure 3.1)<sup>8</sup>. To this base resin is added from 20 to 40% plasticizer content by weight. This plasticizer can be any number of adipate, phosphate and phthalate compounds which are compatible with PVB in ratios up to 1:1 by weight.<sup>8</sup> Trace proprietary additives including ionic salts are further compounded with the polymers to tailor the properties for a specific application.<sup>3</sup>

The interlayer material is bonded between two sheets of glass to form laminated safety glass. The thickness of the glass depends on the application as does the thickness of the interlayer. Commercial PVB interlayer material is available from 0.038 cm to 0.152 cm thick.<sup>3</sup> Of these, 0.076 cm is the most common. The layers are laminated together with pressures of 1.3 to 1.4 MPa at temperatures of 140°C for 30 to 120 minutes.<sup>2</sup>



**Figure 2.1.** Chemical Structure of polyvinylbutyral. X represents the number of vinylalcohol groups in the backbone. Y represents the number of vinylalcohol groups and z represents the residual vinyl acetate functions.

### 2.2.1 Structural Analysis

The morphology of a polymer is directly related to its mechanical properties. For example, thermoplastic semi-crystalline polymers are stiffer and stronger than their non-crystalline counterparts as a rule. More important to this work is the effect of multiple phases within a material on its impact energy absorption characteristics. Polyethylene containing both crystalline and amorphous phases is an extremely tough material due to the viscous liquid-like mobility of the amorphous regions which are above the glass transition temperature of the polymer.<sup>11</sup> This same principle is used in rubber toughened epoxies where the energy absorbent rubber phase blunts crack growth in the more brittle epoxy regions under load.

PVB is a thermoplastic amorphous polymer with a complex multiphase morphology. Parker, *et al* have studied the phase morphology of both neat and plasticized PVB.<sup>12</sup> They found that both materials have at least two phases with the existence of more phases possible. Schaefer *et al*<sup>13</sup> also studied the structure of PVB plasticized with different levels of Dihexyladipate (DHA) from 0 to 32 parts-per-hundred (phr). They found that at even low levels of DHA, phase segregation occurred. The resulting material contains both hard and liquid-like soft segments. The degree of phase separation and amount of each phase was affected by the residual hydroxyl content of the resin.

Further work by Parker *et al* explored the effect multi-phase behavior has on dynamic mechanical properties.<sup>14</sup> Using PVB plasticized with 32 phr of DHA they discovered a beta transition peak at -47°C and two  $\alpha$  peaks, one at 12°C and one at 31°C. Further tests above the glass transition temperature using PVB laminated to a fiberglass braid showed yet a third transition, designated  $\alpha'$  at 95°C. DSC analysis of this material shows the presence of three glass transitions as well, one at -5.7°C, one at 8.9°C and one at 45.3°C. The existence of separate glass transitions was explained as resulting from the multiphase nature of the material. The lower transitions temperatures would be associated with the soft, liquid-like regions described by both Schaefer<sup>13</sup> and Parker<sup>14</sup>.

This multiphase morphology is indicative of the impact strength and tear resistance of plasticized PVB. In either situation the soft phase would tend to blunt cracks and absorb energy. In static loading conditions, the 'hard' phase would provide the strength, with the soft phase serving to blunt any cracks which do form thus increasing the tear strength.

## 2.3 Mechanical Properties

Neat PVB, sold as Butvar by Monsanto Co. has the following typical properties:

**Table 2.1.** Typical Butvar Properties<sup>8</sup>

Molecular Weight (kg/mol)	:	40-250
Tensile Strength (MPA) - Yield	:	40-54
- Break	:	32-55
Elongation (% strain) - Yield	:	8
- Break	:	70-110
Modulus (MPA)	:	1930-2340

Monsanto Company also supplies plasticized PVB under the trade name of “Saflex”™. Saflex™ comes in many forms tailored for the application.<sup>2</sup> Saflex TG™ used for automotive windshields with a plasticizer content of approximately 20% has the following nominal properties:

**Table 2.2.** Typical Saflex TG properties.<sup>2</sup>

Tensile Strength (MPA) - Yield	:	23
Tensile Elongation (% strain)	:	250
100% Modulus (MPA)	:	3.4
Poisson’s Ratio	:	0.5

Saflex™ used for architectural laminates has the following properties

**Table 2.3** Typical properties of Saflex used in architectural glazings<sup>14</sup>

Tensile Strength (MPA)	:	24
Tensile Elongation (% strain)	:	330

These properties were determined at room temperature and at a constant strain rate. As a thermoplastic polymer, PVB is highly sensitive to temperature and rate effects which must be taken into account when designing a laminate for a given application. This rate/temperature effect information is lacking in the product literature.

Some published research has begun to address the time-temperature dependence of PVB.<sup>4</sup> In 1980, Monsanto announced that the plasticizer it had been using in its interlayer material for aircraft windshields would no longer be available. This prompted an in-depth study of comparable plasticizer materials which would pass FAA requirements. These included tensile tests at a constant strain rate but three different temperatures. Similar tests were also carried out for tear strength, stiffness, creep resistance and laminate adhesion. These battery of tests demonstrated the effect of temperature on plasticized PVB. As temperature increased the material becomes softer and more elastic. These tests were all carried out at one plasticizer content and at a single standard test rate.

A decade earlier, J. A. Hooper studied the combined effects of sustained loading, temperature and plasticizer content.<sup>6,15</sup> Hooper used hard and soft interlayers with the principal difference being plasticizer content. These formulations were tested at three different temperatures: 1.4 °C, 25°C, and 49°C. Using a four point bending creep test to determine sustained loading properties, he determined that PVB is essentially a viscoelastic fluid with laminate properties approaching that of unbonded sheets at high-

temperatures and long times. Fatigue tests were also carried out on laminate constructions with no inherent loss in laminate strength discovered. Full scale burst pressure testing was also carried out at ambient conditions which verified the retention of structural integrity after failure of both inner and outer glass panes.

There is a large body of work published concentrating on the behavior of laminated safety glass as a whole.<sup>16,17,18,19,20,21</sup> These research efforts are concentrated on the performance of the whole composite and do not consider how differences in interlayer properties affect the composite. Some high temperature work was done, but no complete study of how load rates and test temperatures affect laminate properties.

More recent research by Vallabhan *et al*<sup>22</sup> has attempted to bridge the gap between interlayer properties and laminate characteristics. This work sought to characterize the static shear stiffness of PVB as laminated, with the ultimate goal of developing a model for laminate behavior. Again, only one material formulation was used and the tests were essentially static, severely limiting the usefulness of the study.

### **2.3.1 Dynamic Properties**

The research cited above was primarily concerned with the properties of PVB at one strain rate. PVB is viscoelastic however, with mechanical properties that depend on temperature and rate of loading. This behavior has been addressed to a certain extent for aircraft windshields. A. Jayarajan<sup>23</sup> studied the dynamic behavior of PVB plasticized with either 3GH or AG2 using Dynamic Mechanical Analysis. This technique allows



testing at frequencies ranging from 0.1 Hz to 100 Hz and the possibility of varying the test temperature. By testing over a range of temperatures at the given frequencies and applying time-temperature superposition, it is possible to generate a master curve extending over a much broader range of frequencies at a given temperature than can be directly studied. In this fashion, the adequacy of an interlayer material to perform under widely varying test conditions can be better understood. For example, load transfer ability at low strain rates and high temperatures can be determined. From the same data, energy absorption characteristics at impact velocities and low temperatures can also be analyzed.

Such dynamic experiments provide a more complete understanding of material properties than static loadings. This is particularly important in studying and determining the suitability of a material under impact loading conditions. Although impact conditions are not well characterized, impact loadings can be considered as a high frequency loading. Therefore, the high frequency behavior of a material at a given temperature is critical in determining how the material will perform during impact. By evaluating the mechanical behavior of the polymer over a range of frequencies and temperatures, it is possible to generate a master curve using time-temperature superposition. This curve would cover a broad range of frequencies including the high frequency range associated with impact behavior. Laminate impact tests are important tools in certifying a construction and provide valuable insight into the interactions

between each of the individual components. But without adequate characterization of each component, it will be very difficult to design a structure with improved penetration resistance or energy absorption.

## 2.4 Adhesion

There are many viewpoints concerning why two materials or structures bond together. In the textile industry, mechanical interlocking is the primary mechanism. This same mechanism holds true for many porous substrates. Between two planar materials, other interactions must occur for strong adhesion to occur. These include acid-base interactions, hydrogen bonding, chemical crosslinking, Van der Waals forces, interdiffusion and electrostatic forces among others.

Monsanto Europe SA contends that moisture content is the most important factor in determining glass/PVB adhesion.<sup>2</sup> Adhesion has been attributed to the presence of unreacted hydroxyl groups in PVB which form the bond with glass. At the same time, Monsanto Company, in their product literature, claim that it is the substitution of butyral groups for acetate groups which increases the adhesion between PVB and various substrates.<sup>8</sup>

The effect of surface roughness on PVB/glass adhesion was studied by Chugonov *et al*<sup>24</sup>. They determined that an increase in surface roughness decreased the amount of adhesion. This implies that mechanical interlocking does not play a role in PVB/glass adhesion.

Watts and Chehimi<sup>25</sup> discuss PVB adhesion in terms of acid-base interactions which would occur between soda-lime glass and PVB. Huntsberger<sup>26</sup> used the presence of ionic salts to control the moisture content in the interphase and concluded that the

presence of moisture greatly lowers the PVB/glass adhesion. This method of adhesion control is apparently practiced commercially. David and Misra<sup>27</sup> suggest that PVB interlayer materials contain small amounts of ionic salts which allow tailoring of the adhesive properties of the interlayer for a given application.

Understanding the mechanism of adhesion first requires a method of measuring the bond strength. Some of the more common methods include butt joints, lap shear tests, and peel tests at 0, 45, 90, 180 degrees and any angle in between. A popular method for measuring membrane adhesion is the blister test.<sup>28</sup>

Some interesting work analyzing the use of the blister test has been done by Lai and Dillard<sup>29</sup> in recent years. They discuss a “fracture efficiency parameter” which is defined as the ratio between the strain energy release rate and the square of maximum stress. The goal of this work was to determine a means of avoiding sample yielding during the test to obtain more accurate strain energy release rates. Their results suggest that yielding occurs regardless of the blister geometry at the same applied strain energy release rate for a given film.<sup>29</sup> Lai and Dillard<sup>30</sup> have also studied a number of other test geometries and applied this theory of fracture efficiency. They suggest that this parameter is useful in determining if yielding will occur and whether elastic or elasto-plastic analysis is required.

The most popular test for flexible adhesives or substrates is the peel test. The primary benefits include low cost, fast testing and readily available equipment. Most

peel tests are typically carried out using a tensile testing device and either a T-peel configuration or some type of moveable clamping device to maintain a constant peel angle. For quantitative and accurate measurement of the work of adhesion, this test method has several drawbacks. Regardless of peel angle, some amount of yielding will occur in either the substrate or more likely the adhesive. Yielding of either component will alter the strain energy release rate. Secondly, the size of the peel angle will change the failure mode mix. Typically, peel test geometries create a mix of Type I opening mode and Type II shear failure modes. The more shear, the more likely yielding will occur with correspondingly higher measured peel strengths. However, the peel test is well suited for purely qualitative comparisons of the adhesive strength between two materials or formulations.

David and Wittberg<sup>31</sup> used 90° peel tests to measure the adhesion of PVB to glass. They discovered using ESCA analysis that the samples failed cohesively with a thin layer of polymer remaining on the surface. The thickness of this layer was found to be directly related to the force of adhesion. David and Misra<sup>27</sup> discovered the same phenomenon using surface contact angle measurements. No mention is made in either article of the peel rate or test temperature but from the description of the ESCA measurements, the test temperature can be assumed to be 25°C. In order to make accurate comparisons between specimens, it is likely that a constant peel rate was used.

As mentioned in the previous section, the properties of PVB are dependent on temperature and load rate. This dependency will affect the measured bond strength of the interlayer to a glass substrate. By examining this time-temperature dependence, a more complete understanding of PVB/glass adhesion can be achieved.

Andrews and Kinloch<sup>32</sup> have used time-temperature superposition to generate master curves of the strain energy release rate, ( $G$ ), versus the crack growth rate, ( $\dot{a}$ ), for crosslinked rubber. Using the Williams-Landel-Ferry equation, a single relation between the critical strain energy release rate, ( $G_c$ ), crack growth rate and temperature can be produced for testing above the  $T_g$  of the material. Similar work has been done on uncrosslinked SBR.<sup>33</sup> The experiments ranged over a temperature range of  $-35^\circ\text{C}$  to  $+60^\circ\text{C}$  indicating a broad leathery region above the  $T_g$  for SBR. Again, the test data from each temperature was adjusted to fit a master curve using the WLF equation.

The resulting data provides insight into the effect of temperature and rate on the failure mechanisms and consequent energy release in the system. The resulting master curve was broken into two parts, the lower portion associated with low crack growth rates and/or high temperatures governed by cohesive failure in the adhesive. This is due to the fracture stress of the adhesive being less than the maximum interfacial stress. The second region at higher strain rates and/or colder temperatures is associated with interfacial failure between the adhesive and the substrate. It is this second region which

is of most interest for research into the strength of the bond between adhesive and substrate.

## 2.5 Photoageing

Carbon based polymers, like other materials, are susceptible to degradation under certain conditions. These conditions include chemical attack, thermal degradation, thermo-oxidative effects and light radiation ranging from UV through visible to IR. This degradation will change the properties of the polymer beyond that intended by the designer. It is this durability challenge in a given environment which must be met by the designers of a structure containing organic polymers.

Laminated safety glass is one such structure which is commonly used in applications where it will be subjected to direct sunlight for long periods of time. These include automobile windshields and architectural glazing where exposure typically occurs over a period of years. For this reason, it is important to understand how the components of laminated glass, namely the organic polymer interlayer, will be affected by UV radiation present in sunlight.

Monsanto Company has determined that the glass used in architectural glazing approximately 3 mm thick typically absorbs 100% of radiation below 310 nm. This protection drops to below 20% at 360 nm.<sup>34</sup> They have further shown that plasticized PVB absorbs 100% of the radiation up to 375 nm and higher. Upon interaction with the interlayer, the energy must either be converted into heat, absorbed in chemical reactions occurring within the polymer, or transmitted through.



Mikhailik *et al*<sup>55</sup> have studied the mechanism of photoageing and concluded that PVB may either crosslink or chemically disassociate depending on the wavelength of light and temperature. This study involved unplasticized PVB.

The cross-linking or chemical disassociation found by Mikhailik *et al*<sup>55</sup>, if present in large enough quantities will change the mechanical properties. Saad, *et al*<sup>56</sup> have studied the effect of UV photoirradiation on the dielectric and dynamic mechanical properties of low molecular weight PVB. They showed that the polymer formed a cross-linked network with a corresponding increase in the glass transition temperature. This study used PVB which was significantly different from that typically found in safety glass. The correlation between these results and the effect of UV radiation on typical safety glass materials is uncertain because of the difference in molecular weight, (Saad, *et al*<sup>56</sup> used 36000 Mw whereas Saflex is typically on the order of approximately 100,000 Mw) and the lack of a plasticizer.

Research into the effect of UV exposure on the properties of typical safety glass materials has been unfocused. It has often involved PVB which is sufficiently different from that used in laminated glass to make the correlation between the results found and actual behavior of the material to be uncertain. Furthermore, the amount of degrading radiation present in a typical lifespan of a laminated glass unit has not been well categorized to provide a guide for further ageing studies.

## III. EXPERIMENTAL SECTION

### 3.1 Sample Preparation

Polyvinylbutyral in powder form with a  $M_w$  of 180,000 to 270,000 g/mol was obtained from PolySciences, Inc. The solvent used to plasticize the polymer was butyl benzyl phthalate obtained from the Monsanto Co. as Sanitizer 160.

Solution casting was used to generate films with 0, 10, 20, 30 and 40% plasticizer content by weight. The appropriate amount of neat polymer powder and Sanitizer 160 were added to a mixture of 40% Toluene and 60% Ethanol and mixed for 24 hours using a magnetic stirring rod and plate. The solution was cast onto glass plates cleaned with a mild detergent soap. For films that were to be later used in peel or blister samples, the glass plates were cleaned with a mild detergent soap and rinsed with deionized water. Thin films (0.04 to 0.08 mm) were cast using a 2% polymer solution. The films were allowed to evaporate at room temperature for 1 week prior to any testing or ageing.

Thicker films (0.2 to 0.4 mm) were cast using a 10% polymer solution to be later pressed together to form the required mechanical evaluation samples. The solvent was allowed to evaporate at room temperature for 2 days. The films were then placed in an oven at the expected final Tg of the plasticized PVB. This temperature was gradually increased over a period of 24 hours to 20°C above Tg and remained at this elevated temperature for a further 48 hours. Each film was then removed from the glass plates. Films with a plasticizer content greater than 20% were frozen to facilitate removal.

### **3.2 FTIR Spectroscopy**

Fourier Transform Infra-Red Spectroscopy (FTIR) was performed on thin films of PVB using a Nicolet 750SX FTIR Spectrometer in transmission. Initial samples were taken from the films 1 week after casting. The films were then photoaged as appropriate. Samples were periodically removed and analyzed during ageing. The spectra that were collected on these aged samples were then compared to the original unaged material.

### 3.3 Mechanical Testing

Tensile test samples (0.7 to 0.8 mm thick) were obtained by pressing cast films together in a Carver hot press at 140°C and 1.1 MPa. Samples were diecut from these films in a dogbone shape with a 10mm gauge length and a width of 2.5 mm. The samples were tested using a Polymer Laboratories Miniature Materials Tester equipped with either a 200 N or a 20 N loadbeam. Each load beam has been calibrated to within 1% accuracy. Tensile tests were performed with deflection rates varying between 0.1 and 99.99 mm/min. For all tensile experiments, the distance between the grips was used as the initial length instead of the gauge length of the die since a significant amount of strain was evidenced in the curved region of the sample. Strain values reported are engineering values taken as  $\Delta l/l$ . Engineering stress is reported as the load over initial cross sectional area.

### 3.4 DMTA

Dynamic mechanical thermal analysis of both aged and unaged mechanical samples was performed on a Polymer Laboratories Mark II DMTA. The samples were loaded in a double cantilever beam configuration with the ends firmly clamped and the middle oscillated by a controlled moving beam. The maximum deflection of the sample was fixed by the sample dimensions. The samples were loaded into the unit at room temperature and cooled to  $-90^{\circ}\text{C}$  and firmly tightened.

Data was taken every  $2^{\circ}\text{C}$  at frequencies of .1, .33, 1, 3.3 and 10 Hz. By measuring the phase angle difference between the loading curve and the deflection, the storage and loss components of the bending modulus can be decoupled. These are reported in the form of  $E'$ , the elastic bending modulus and  $\text{Tan } \delta$ , the ratio of  $E''$ , the loss modulus, to  $E'$ . The glass transition temperature reported was taken to be the peak of the  $\text{Tan } \delta$  curve with respect to temperature.

### 3.5 Peel Test

Peel samples (0.7 to 0.8 mm thick) were obtained by laminating dried films onto prepared glass substrates at 140°C and 1.4 to 1.7 MPA. The glass was prepared by scrubbing with a sponge and a mild soap solution, then rinsing with deionized water. The glass was allowed to dry and heated in the press prior to lamination. After pressing, the adhesive strips were cut to 1 inch wide widths and photoaged as appropriate. After ageing, a Kapton backing was affixed to the samples using a thin layer of two part epoxy resin. To improve bonding between the backing and the PVB, both surfaces were sanded prior to lamination. The epoxy was allowed to cure for a period of 16 hours.

The equipment used to perform the peel experiments was a load controlled peel test machine designed and built here at Va Tech (Figure 3.3). The strip of PVB was peeled from the glass substrate using the beam setup depicted. By suspending a weight from the beam (W) a force was applied to the sample through the load rod attached to the Kapton/epoxy backing.

During a normal experiment the sample is clamped to the sample stand. Depending on which way the adhesive strip is pulled from the glass, a peeling angle of 45° or 135° can be achieved. Accurate loading of the samples is insured by adjusting the counterweight shown to balance the equipment after each test. This is done with the beam in the horizontal position supporting the unattached adhesive and load rod

assembly so that the load acting on the adhesive comes solely from the suspended weight.

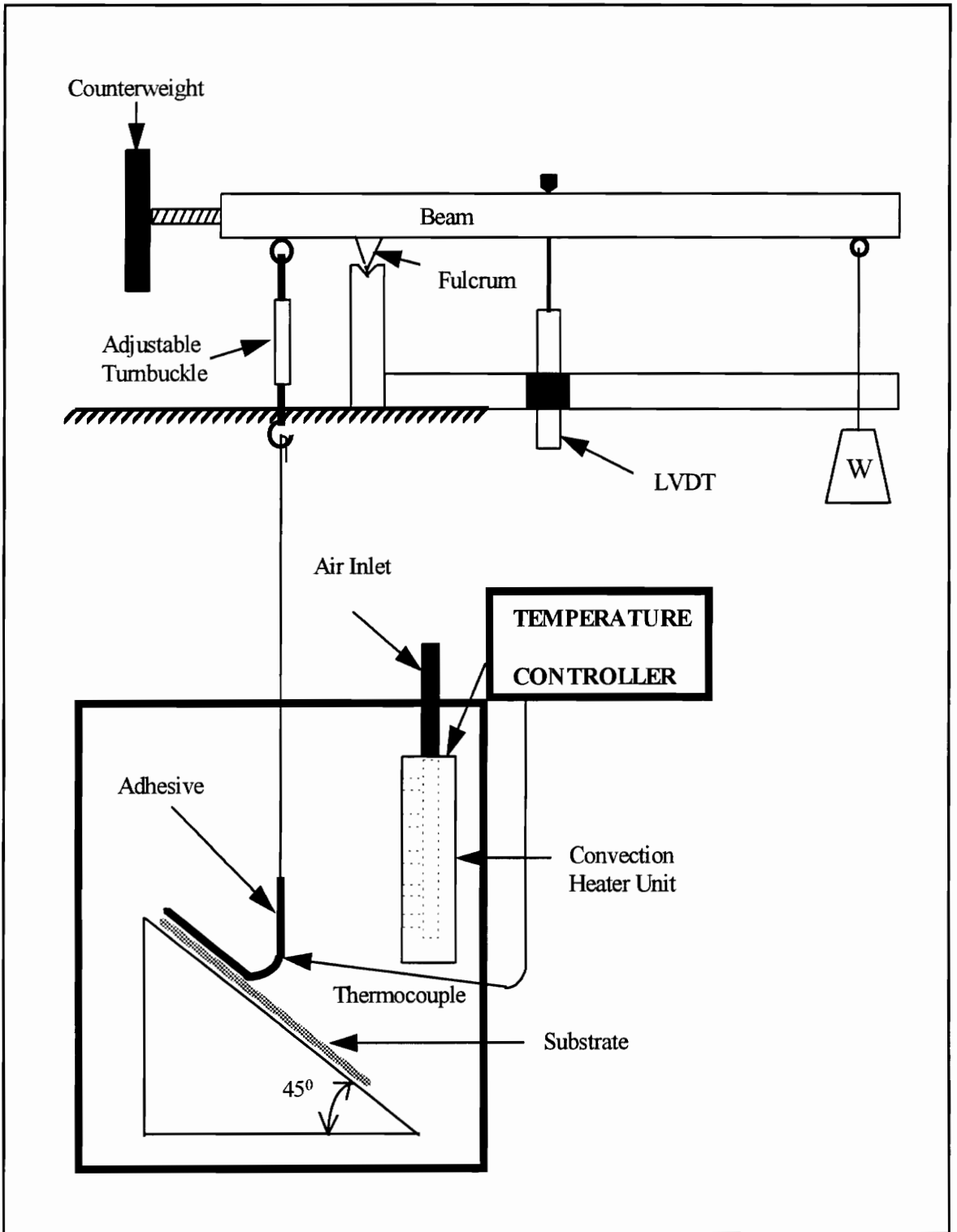
The deflection of the beam, and thus of the adhesive strip, is measured using an LVDT. Assuming the Kapton backing does not creep during the experiment, the rate of deflection of the load beam is directly related to the crack growth rate once steady crack growth is achieved. The beam deflection, as measured using the LVDT, is calibrated regularly with a micrometer accurate to 0.01 mm attached to the supporting structure of the machine. The probe of the micrometer is used to adjust the position of a platform attached to the load rod. Incremental, 0.05 mm displacements of the platform are then correlated with the voltage output of the LVDT.

The relationship between beam deflection and crack growth was calculated as shown in Figure 3.4 and checked using a video camera and timing device during an actual peel test. During a given test, the loadbeam deflects a maximum of  $\pm 5^\circ$  from horizontal resulting in a maximum loadrod deflection of 2.5 mm. This translates into approximately 1 mm of actual crack growth. By adjusting the turnbuckle, multiple measurements can be made for a given load at a given temperature on each specimen.

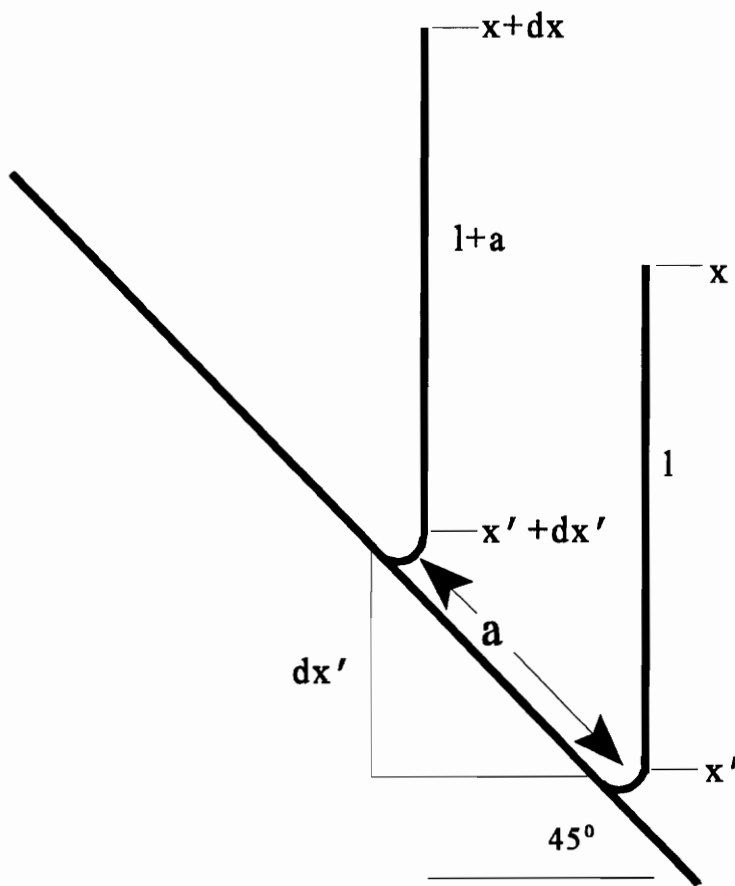
The sample stand is encased in an insulated oven whose temperature is controlled using an Omega CN9000A temperature controller . The input signal comes from a thermocouple attached to the adhesive within 1 cm of the crack front. The controller then applies power to a Firerod™ rod heater embedded in an aluminum block through

which air is forced. The sample temperature can be maintained at  $\pm 0.5^{\circ}\text{C}$  of the set temperature up to a maximum of  $100^{\circ}\text{C}$ .





**Figure 3.1.** Peel Test Equipment.



$dx$  is measured using LVDT

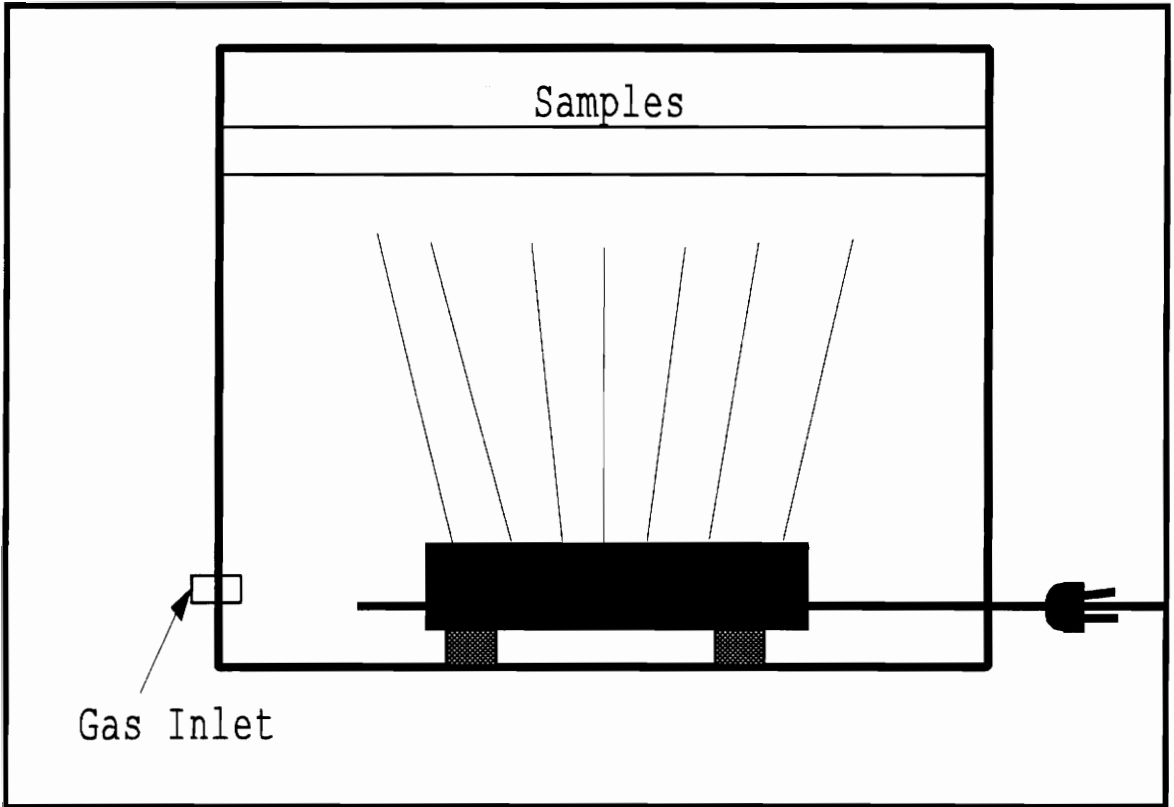
$a$  = crack length

(1)	$dx' = dl \cdot \sin 45^\circ$
(2)	$l = x - x'$
(3)	$l + a = (x + dx) - (x' + dx')$
(3 - 2)	$a = dx - dx'$
(1 subst into 3)	$a = dx - a \cdot \sin 45^\circ$
(simplify)	$a = dx - a \cdot \sin 45^\circ$
(rearrange)	$a = dx / (1 + \sin 45^\circ)$

**Figure 3.2.** Crack growth determination from sample displacement.

### **3.6 Photoageing**

Photoageing experiments were carried out using a Spectroline R51A lamp emitting at 254, 313 and 367 nm . This lamp was enclosed in a sealable wooden chamber (Fig 3.5 UV Chamber). The samples were suspended above the lamp at a distance of 30.5 cm. The samples were either exposed with in an air atmosphere, or with a nitrogen purge gas bleeding into the chamber at the rate of 10cc/min and a pressure of 10 psig. During the inert atmosphere illumination experiments, the chamber was purged for 15 minutes prior to illumination with UV radiation to eliminate the trapped air.



**Figure 3.3.** UV Ageing Chamber

## IV. Chemical Characterization

The chemical structure of neat and plasticized PVB was explored using FTIR spectroscopy. The collected FTIR spectrum of neat PVB is shown in Figure 4.1. The broad peak centered at  $3440\text{ cm}^{-1}$  is associated with the stretching of the O-H bond present in the molecule associated with both residual vinyl alcohol functions and absorbed water. The next set of peaks occurring between  $2850$  and  $3000\text{ cm}^{-1}$  are associated with the asymmetric and symmetric stretching of  $\text{CH}_2$  and  $\text{CH}_3$  groups. The relatively minor peak at  $1735\text{ cm}^{-1}$  is associated with stretching of the C=O bond present in the residual acetate functions. Two strong peaks associated with stretching of C-O-C occurring at  $1137\text{ cm}^{-1}$  and  $950\text{ cm}^{-1}$  can be clearly distinguished in the fingerprint region.

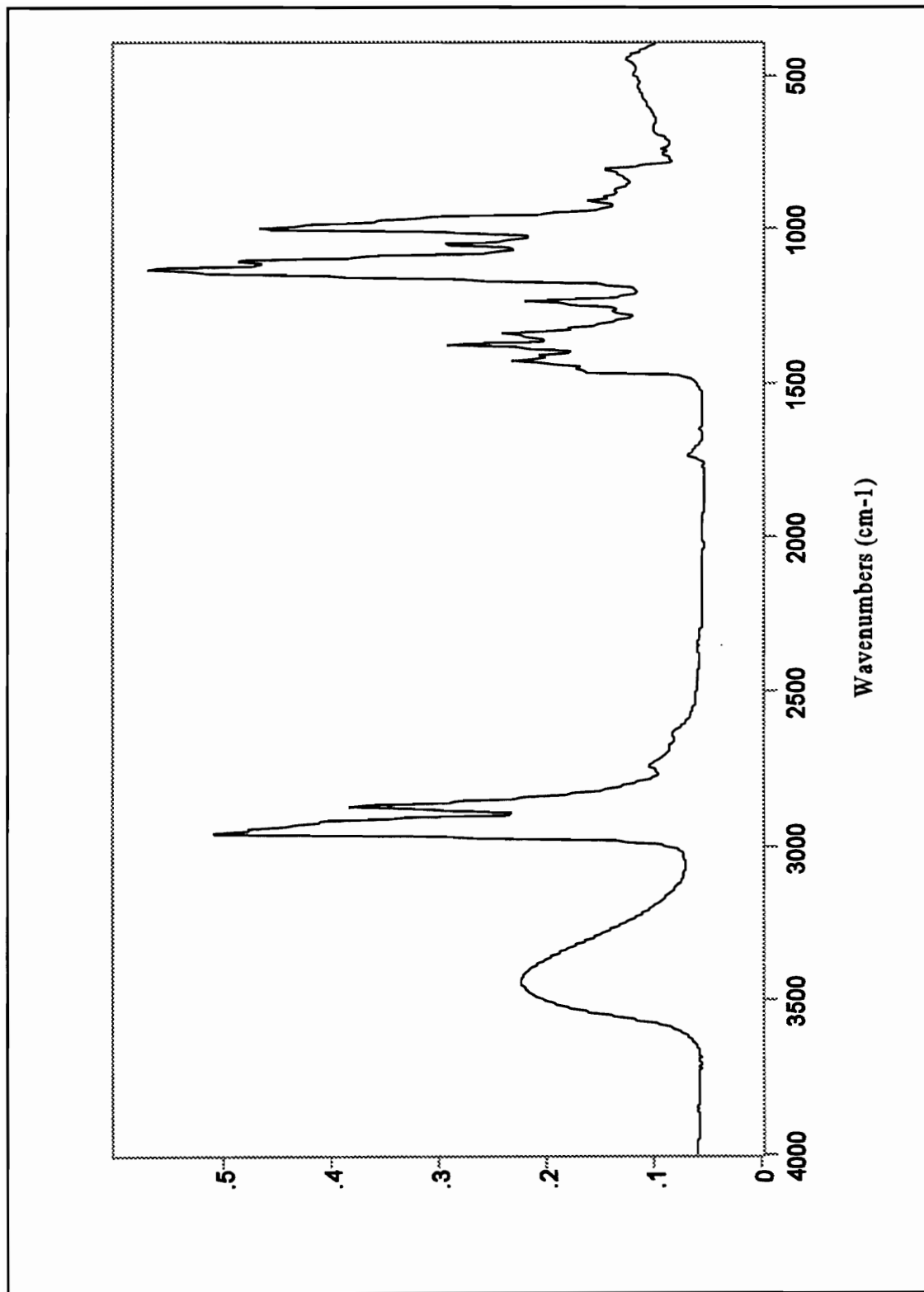
The differences between neat and plasticized PVB are clearly evident when comparing their spectra in Figures 4.1 and 4.2. The small carbonyl peak in neat PVB is replaced by the strong peak at  $1750\text{ cm}^{-1}$  associated with the carbonyl bond found in the plasticizer, butyl benzyl phthalate. Other differences between the formulations can be distinguished in these spectra but for purposes of simple chemical differentiation and characterization, they will not be discussed in detail.

FTIR spectroscopy was also used to track the photodegradation of both formulations as they were subjected to UV radiation. The strength of the peak associated

with the carbonyl bond makes this the most suitable starting place to look for evidence of chemical breakdown of these structures.

Figure 4.3 shows the subtraction spectra of the neat polymer as a function of photoageing time. As the amount of exposure increases, a growth in the peak at  $1735\text{cm}^{-1}$  is readily apparent. Little change is apparent in the sample after 100 hours of ageing. However, the strength of the peak increases dramatically after 200 hours of ageing. The peak does not appear to grow markedly after this first initial jump for the ageing times investigated. Ageing beyond the 600 hours shown embrittled the specimen resulting in destruction of the samples as it was removed from the glass.

The degradation occurring in the plasticized sample is markedly different than that for the neat polymer. Figure 4.4 is a spectra of the aged samples which have had the base/unaged spectra subtracted. This allows a direct observation of the differences between the aged and unaged samples. As in the neat sample, not much activity is seen in the peak at  $1735\text{ cm}^{-1}$  until after approximately 300 hours of photoageing. At this point, the peak splits, with one peak centering around  $1750\text{ cm}^{-1}$  and the other centering around  $1710\text{ cm}^{-1}$ . The amount of splitting continues to increase as a function of photoageing time. This represents the growth of a new species of carbonyl stretching in the aged plasticized sample. The growth of a carbonyl peak in neat PVB and peak splitting in PVB-30 are both indicative of the formation of a carbonyl bond as a function of photoageing.



**Figure 4.1.** FTIR spectrum of neat PVB.

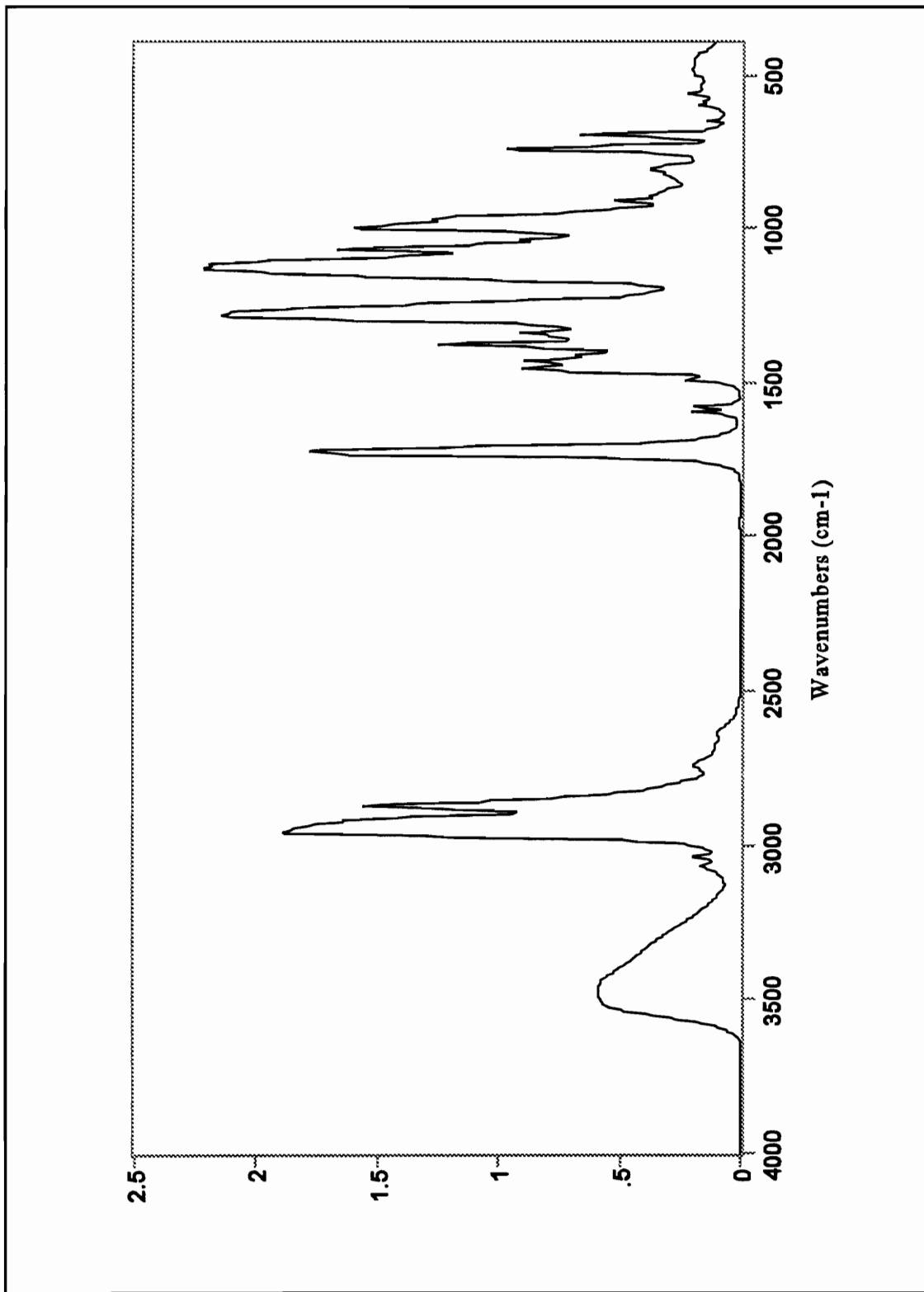
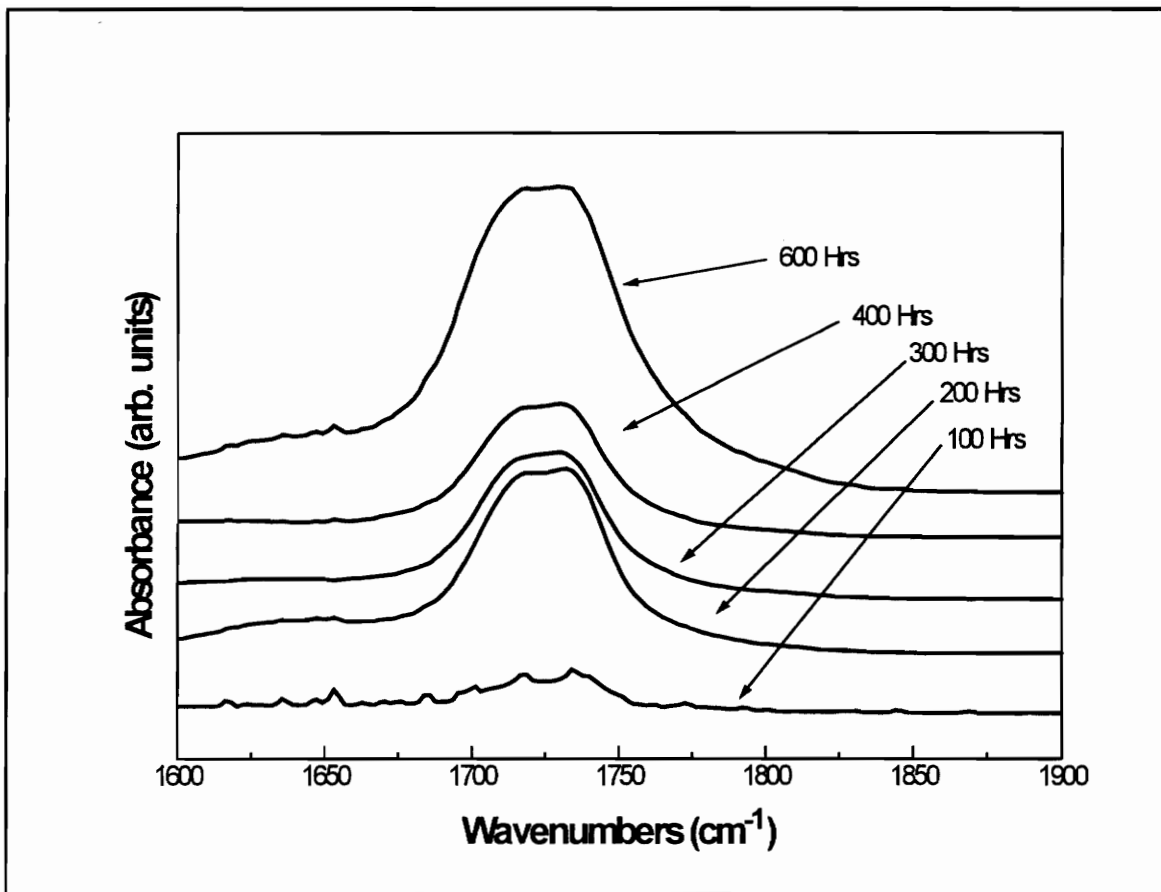
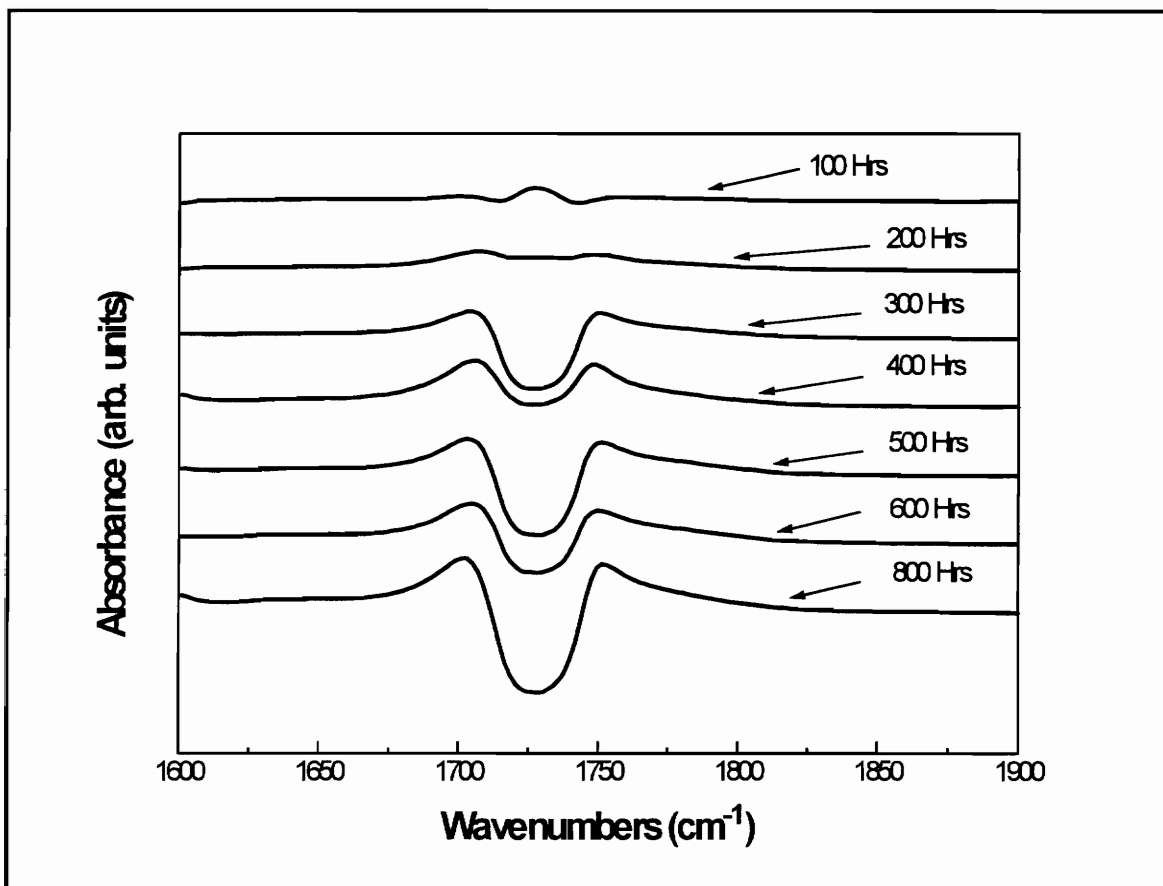


Figure 4.2. FTIR spectrum of PVB-30.





**Figure 4.3.** Subtraction spectra of photoaged neat PVB. Spectra of unaged sample used as base.



**Figure 4.4.** Subtraction spectra of aged PVB-30. The spectra of the unaged samples is used as the base.

## 4.1 Discussion

The growth in the peak at  $1735\text{ cm}^{-1}$  in neat PVB and the peak splitting seen in PVB-30 are both indicative of the formation of a carbonyl bond as a function of photoageing. This is in agreement with the research performed by Mikhailik *et al*<sup>35</sup>. Mikhailik<sup>35</sup> suggests that the increase in carbonyl bonds is due to the opening of the acetal ring structure in the following reaction mechanism(Figure 5.5):

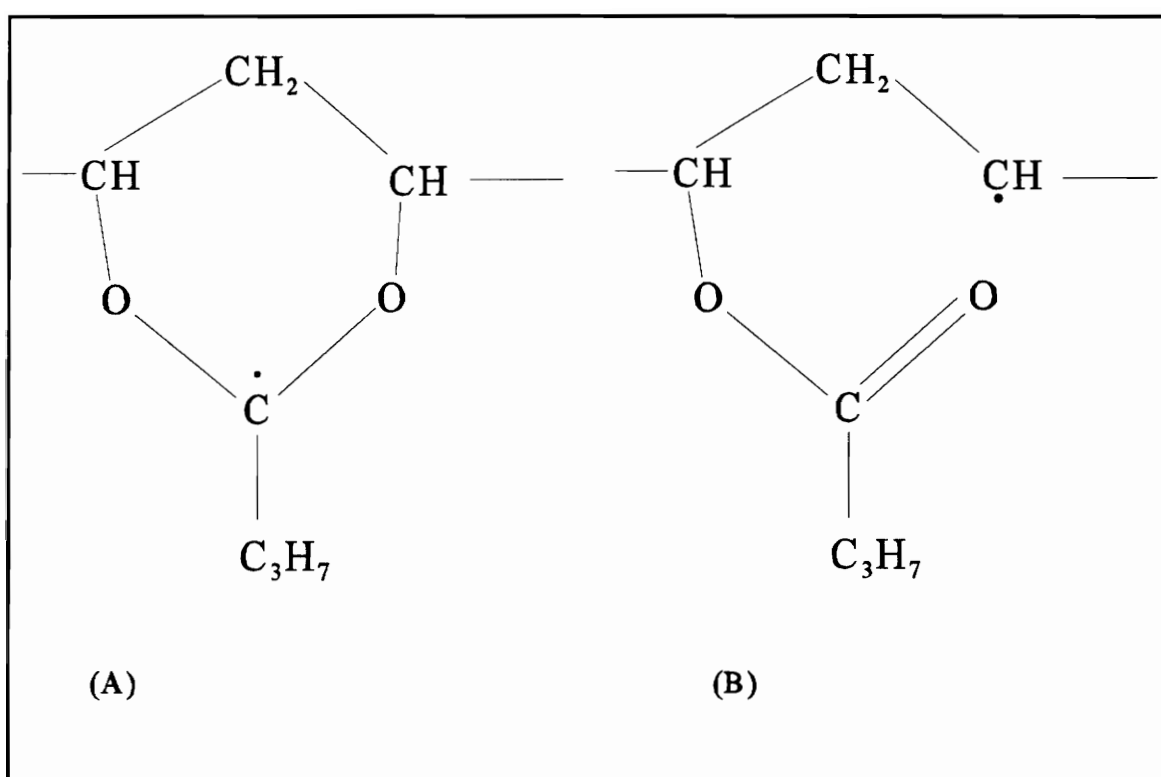


The formation of radical  $\text{R}_2$  is due to UV irradiation at wavelengths between 254 and 313 nm. The shorter the wavelength, the greater the number of generated radicals due to the increase in light absorption by the polymer. Mikhailik *et al*<sup>35</sup> determined that irradiating the samples at room temperature caused a certain percentage of these radicals to react with other chains and form crosslinks. This phenomenon was not evident in the photoaged samples of this study. Both neat and plasticized samples remained completely soluble in tetrahydrofuran at ageing times up to 1000 hours. It is surprising that no evidence of crosslinking was found in the plasticized samples due to the increased mobility of the chains, and ability of the radicals to find sites on other chains.

Another possible explanation of the formation of a carbonyl bond is a reversion of the polymer back to PVAc. Either of these two explanations may occur, and the possibility exists of both results being present in the final structure. Additionally, the presence of a distinct phase morphology in the plasticized sample consisting of



plasticizer rich and polymer rich phases complicates the interpretation. FTIR spectroscopy is not sufficient to distinguish between the different mechanisms and the effect of phase morphology on the result. However, these results have shown that PVB, either neat or plasticized, undergoes photodegradation evident as the formation of carbonyl bonds. The following chapters will discuss the effect this photodegradation has on the mechanical properties of PVB.



**Figure 4.5.** Radicals postulated by Mikhailik *et al* to form during photoaging of PVB. (A) Radical  $R_1$ . (B) Radical  $R_2$ .<sup>35</sup>

## V. Mechanical Properties

### 5.1 DMTA

Dynamic mechanical thermal analysis was performed on samples of neat PVB, PVB-20, PVB-30 and PVB-40 using 5 different test frequencies over a range of temperatures from  $-100^{\circ}\text{C}$  to  $100^{\circ}\text{C}$  where possible. Results for the unaged, neat PVB are shown in Figure 5.1. Increasing the frequency of the test does not change the general behavior of the material, but does change the temperature where transitions occur.

A comparison of the 1 Hz curves of each sample group as a function of plasticizer content is shown in Figure 5.2. As expected, the glass transition region, marked by the rapid loss of stiffness, occurs at progressively lower temperatures as the plasticizer content rises. A second observation is that the transition becomes significantly broader with increasing plasticizer content. This is better seen by examining  $\text{Tan } \delta$  curves in Figure 5.3. The glass transition temperature of each formulation is given in Table 5.1. These values were determined from the temperature at which a peak occurs in the  $\text{Tan } \delta$  curve that is in the same temperature region as a dramatic loss in stiffness evidenced in the elastic modulus.

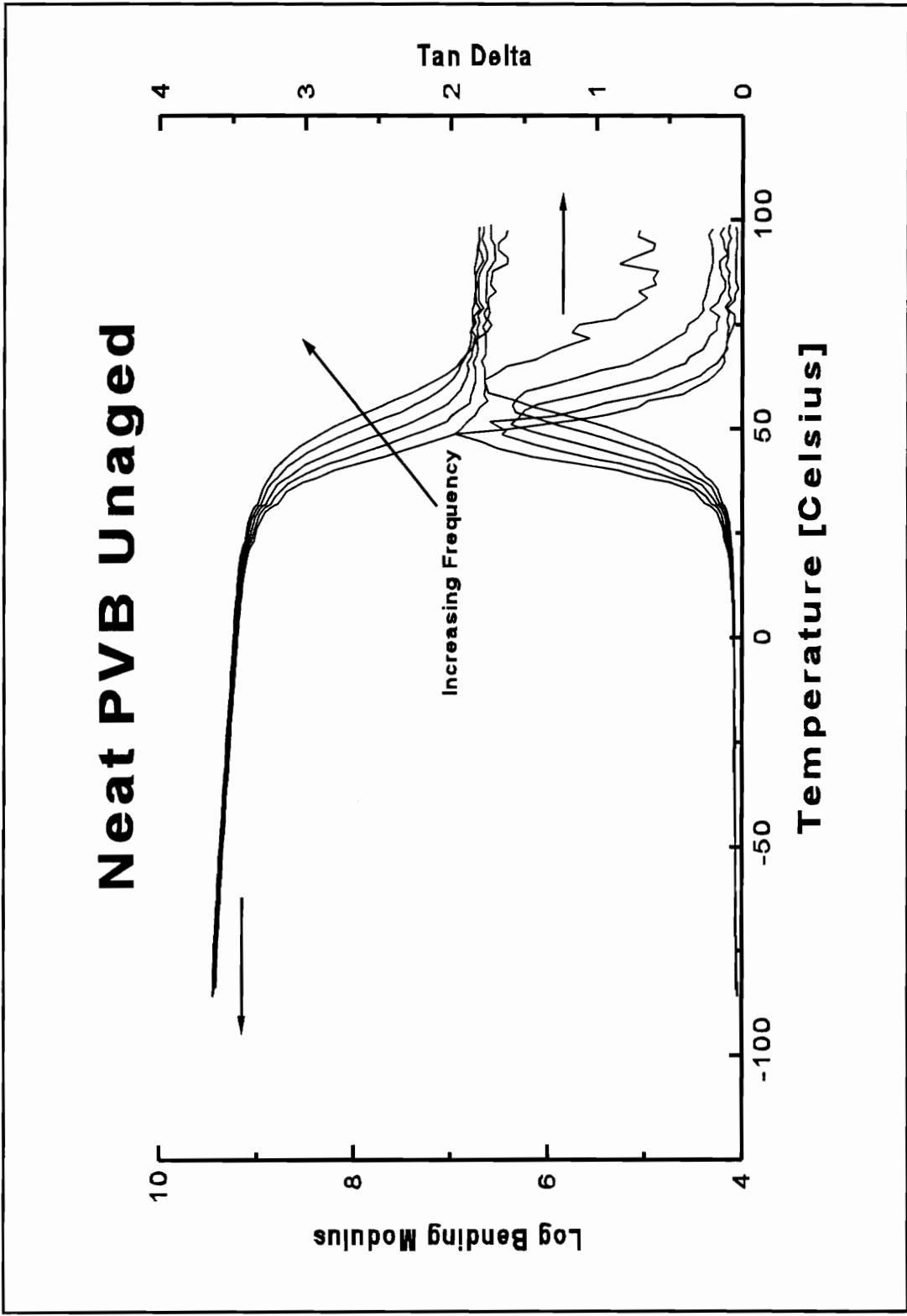
A secondary transition occurs immediately prior to the onset of the glass transition in the more heavily plasticized films. This transition, occurring between  $-40^{\circ}\text{C}$  and  $-10^{\circ}\text{C}$  in each of the formulations, has been commonly associated with a beta transition<sup>14</sup> in the material indicative of localized motion. Because these transitions are

only evident in the heavily plasticized formulations, they may be associated with the plasticizer rich phase postulated by Parker *et al.*

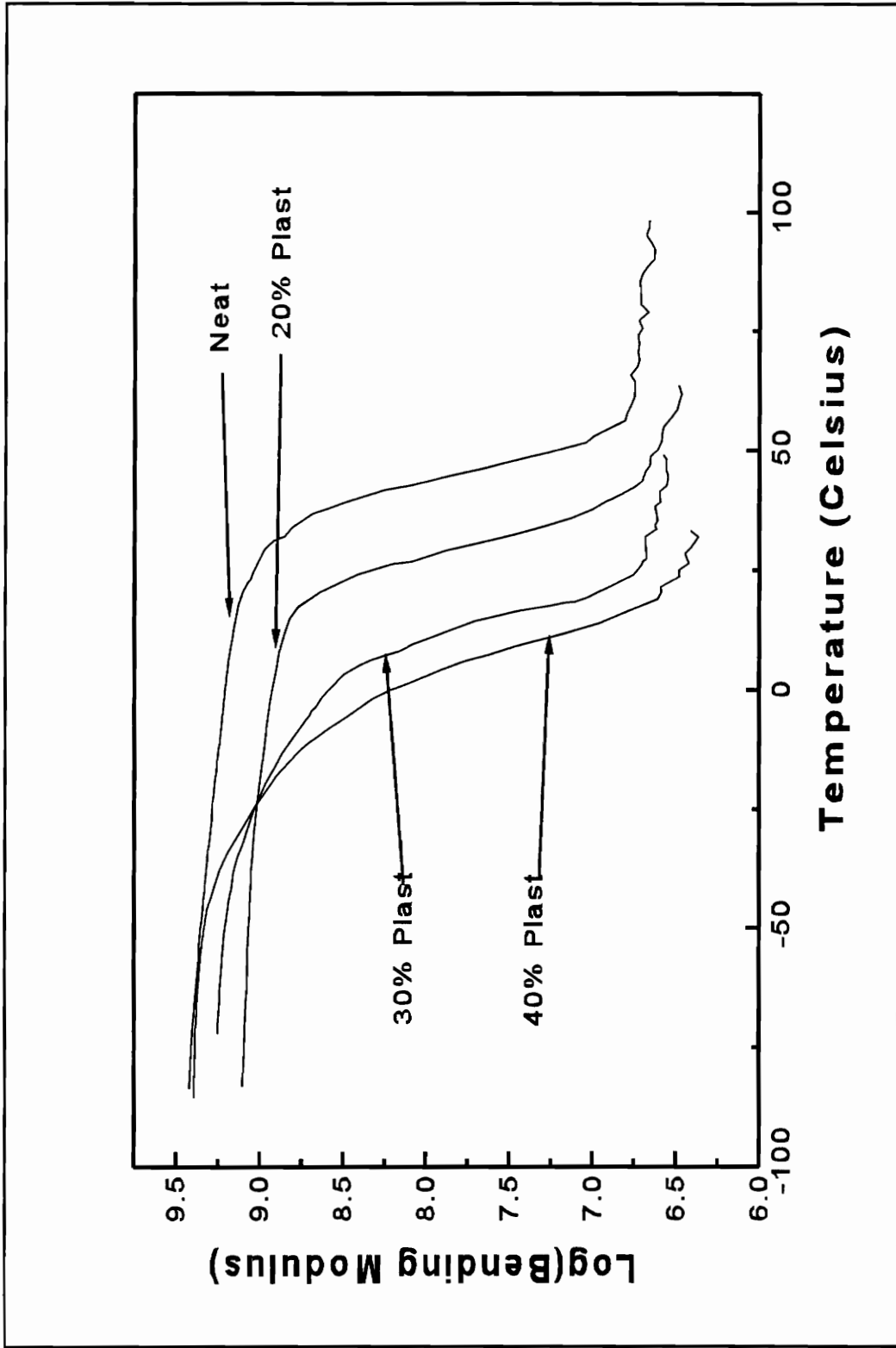


**Table 5.1.** Glass transition temperatures of neat and plasticized PVB as a function of ageing time.  $T_g$  determined by the peak of the  $\text{Tan } \delta$  curve at a frequency of 1 Hz.

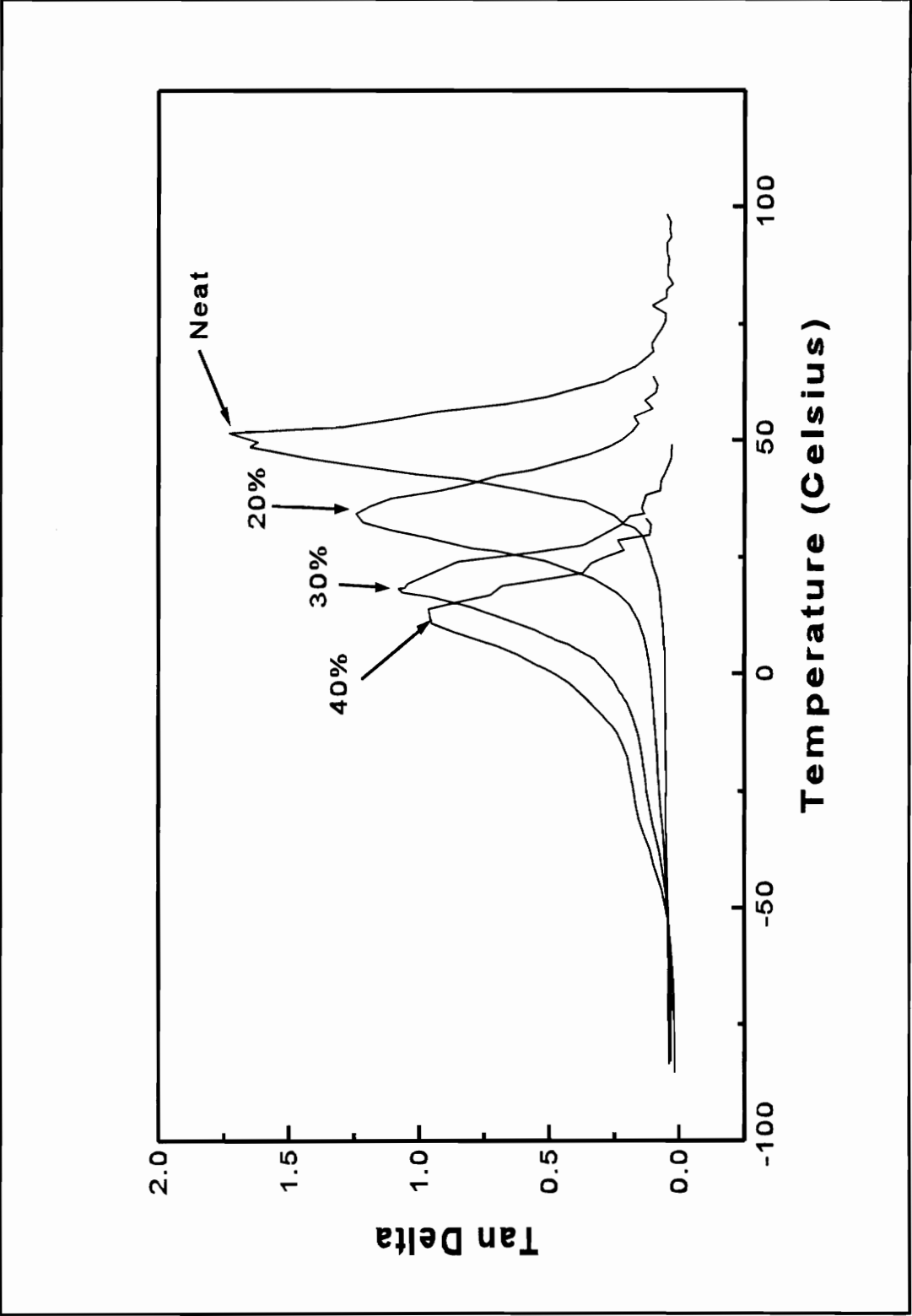
<b>Glass Transition Temperatures</b>				
	<b>Unaged</b>	<b>100 Hrs</b>	<b>250 Hrs</b>	<b>500 Hrs</b>
<b>Neat PVB</b>	50	70	67	70
<b>PVB-20</b>	35	33	36	31
<b>PVB-30</b>	20	22	25	21
<b>PVB-40</b>	13	13	13	13



**Figure 5.1.** Dynamic mechanical-thermal analysis of neat PVB prior to photoaging. The analysis was performed at 5 different frequencies ranging from 0.1 Hz to 100 Hz.



**Figure 5.2.** Visual comparison of the bending modulus of PVB plasticized with different amounts of butyl benzyl phthalate. The results shown are of samples that have not been subjected to photoaging. Each curve represents a testing frequency of 1 Hz.



**Figure 5.3.** Tan Delta values as a function of temperature for unaged samples. Each sample was scanned at the same frequency and the same heating rate.

### 5.1.1 Photoageing Effects

The effect of photoageing on the transitional behavior of neat PVB is shown in Figures 5.4 and 5.5. The entire temperature curve is shown in Figure 5.4. The aging causes a 20°C rise in  $T_g$  (Figure 5.5). The shape of the Tan  $\delta$  peak doesn't change, spanning approximately 30°C in each case.

The differences between the neat polymer and a plasticized sample can be clearly seen in Figure 5.6. A secondary transition occurs in PVB-20 evidenced by the broad peak between -50°C and 10°C which is not present in the neat polymer. This  $\beta$  transition does not change with photoageing. Figure 5.7 is an enlarged view of the glass transition region showing that the peak in Tan delta does not change with exposure. The  $T_g$  for each sample spans approximately 30°C with the peak occurring between 31°C and 36°C.

The  $\beta$  transition occurs in PVB-30 as well, with the same range of -50°C to 0°C (Figure 5.8). Again no apparent change is evident with increasing exposure time. UV exposure does apparently shift the glass transition by 3-5°C (Figure 5.9).

The  $\beta$  transition occurring in PVB-40 is the most pronounced (Figure 5.10). The broad peak occurs in the same region, -50°C to 0°C, but the glass transition region has shifted to a lower degree and the two regions have begun to overlap. Photoageing does not affect the transitional behavior.  $T_g$  for both aged and unaged samples occurs at 12°C (Figure 5.11).

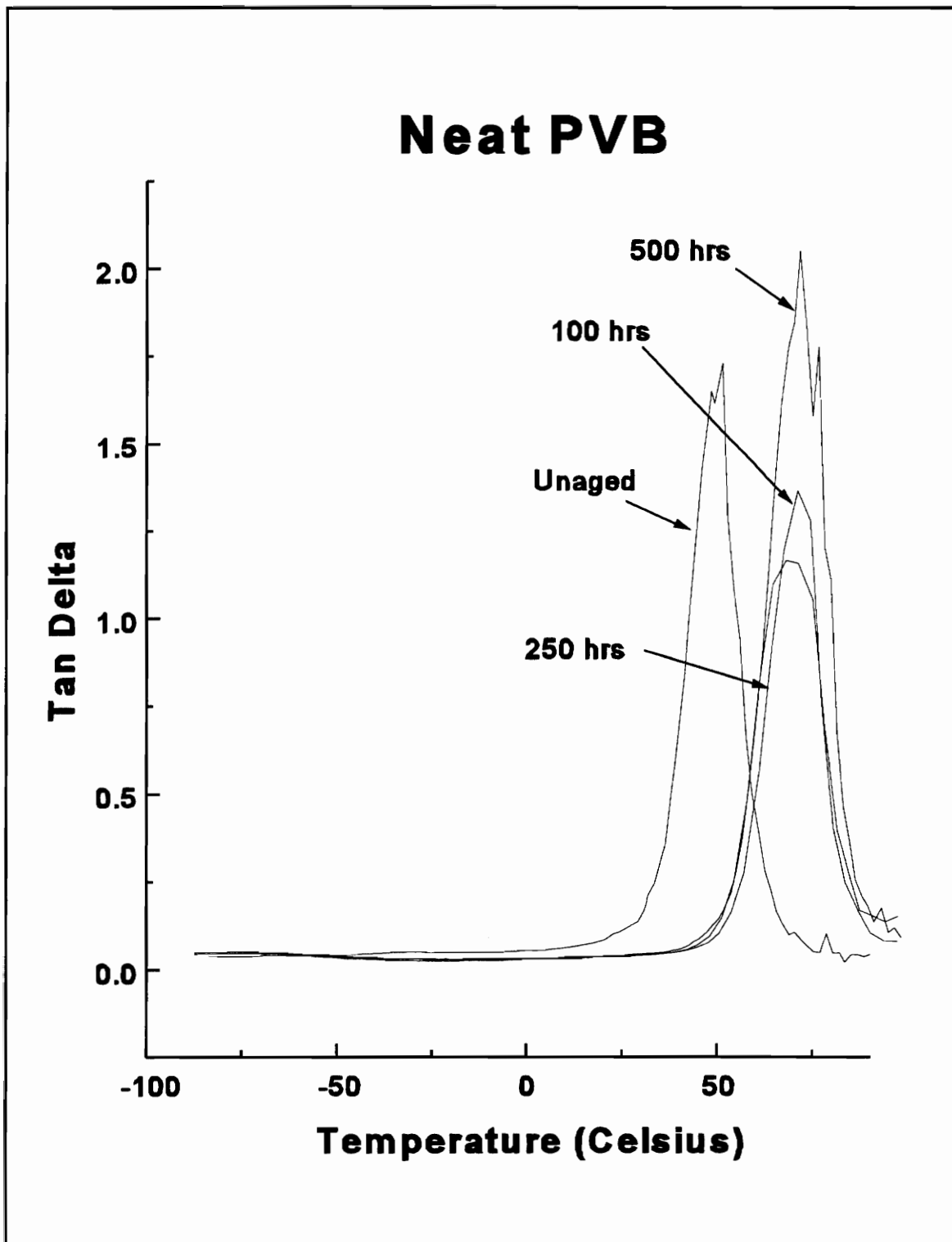
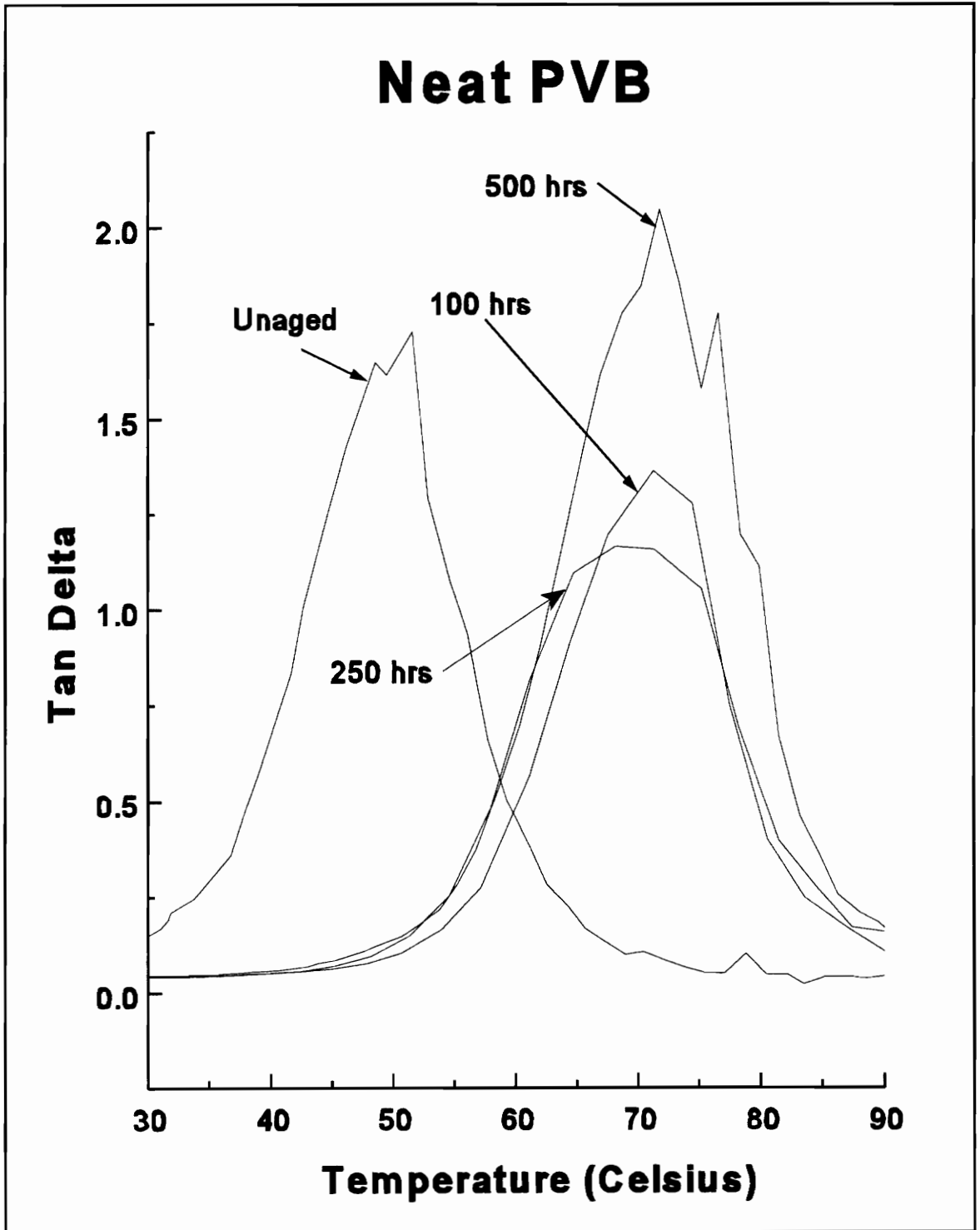
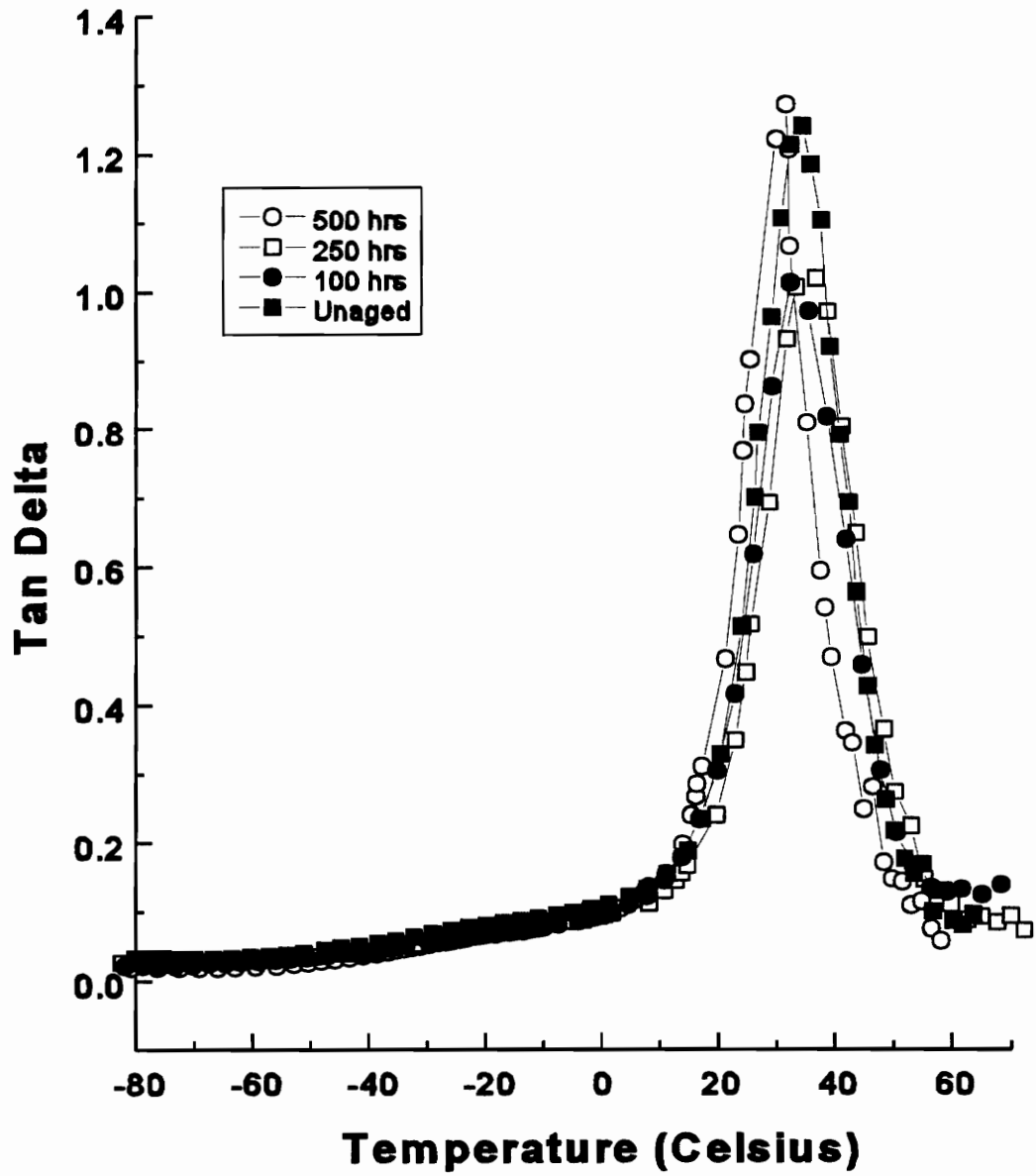


Figure 5.4. Tan  $\delta$  values as a function of temperature for photoaged neat PVB.



**Figure 5.5.** Closeup view of the glass transition region showing the dramatic difference between unaged and aged neat PVB.

## 20% Plasticized PVB



**Figure 5.6.** Tan  $\delta$  versus temperature for PVB-20 showing the effect of photoaging on the glass transition.



## 20% Plasticized PVB

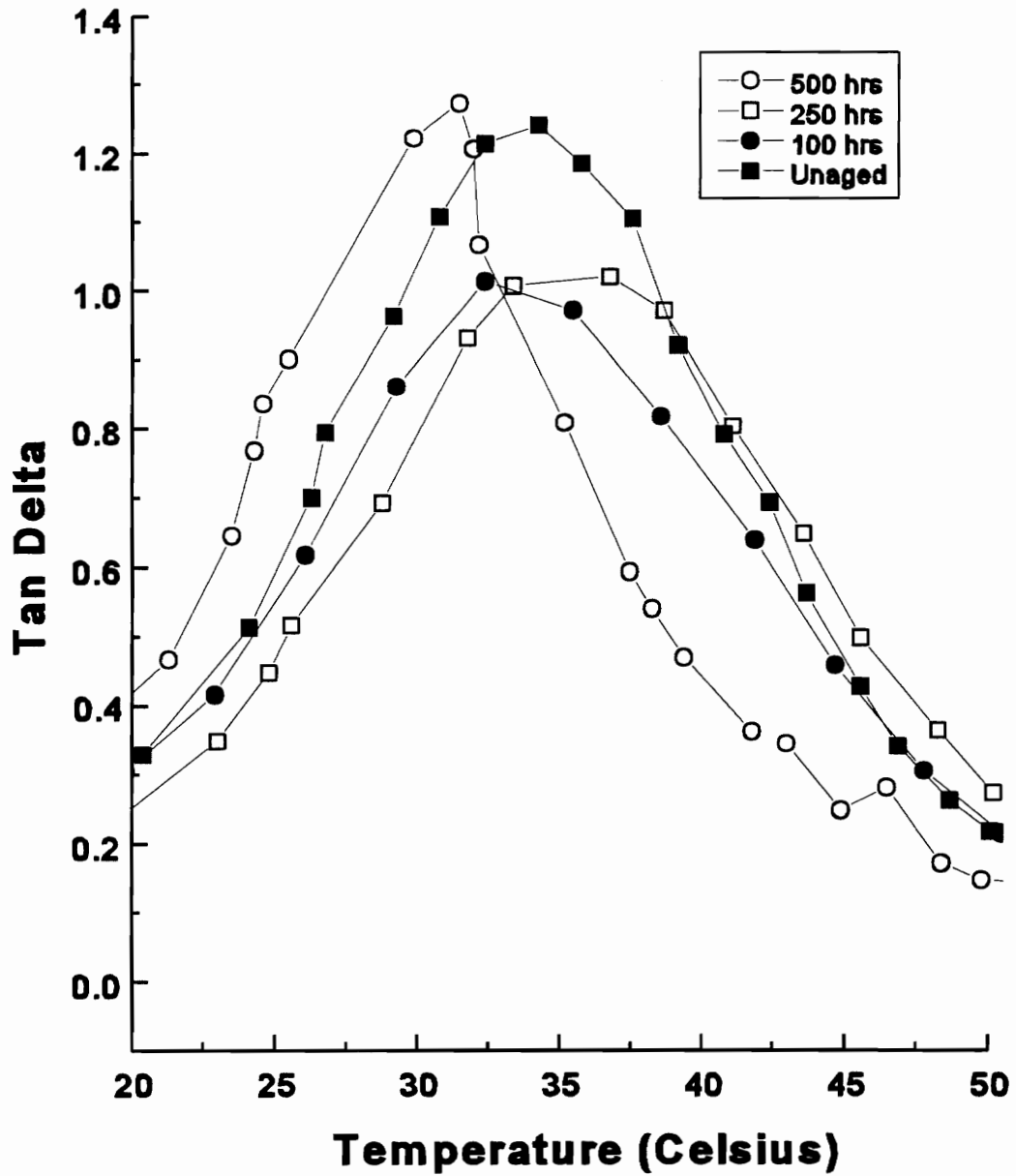


Figure 5.7. Closeup of the glass transition region in a Tan  $\delta$  plot of PVB-20.

## 30% Plasticized PVB

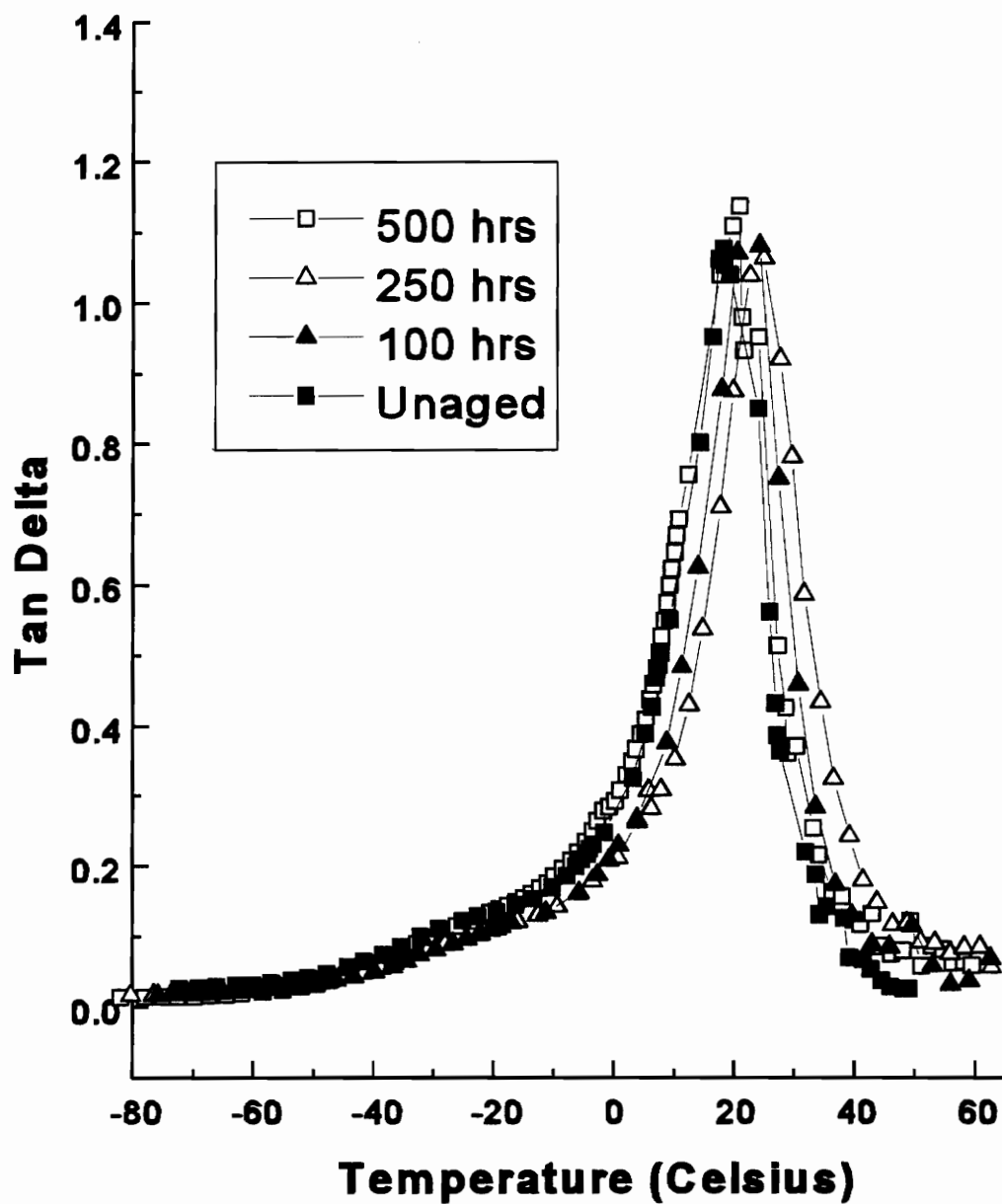


Figure 5.8. Tan  $\delta$  plot of aged and unaged PVB-30.

# 30% Plasticized PVB

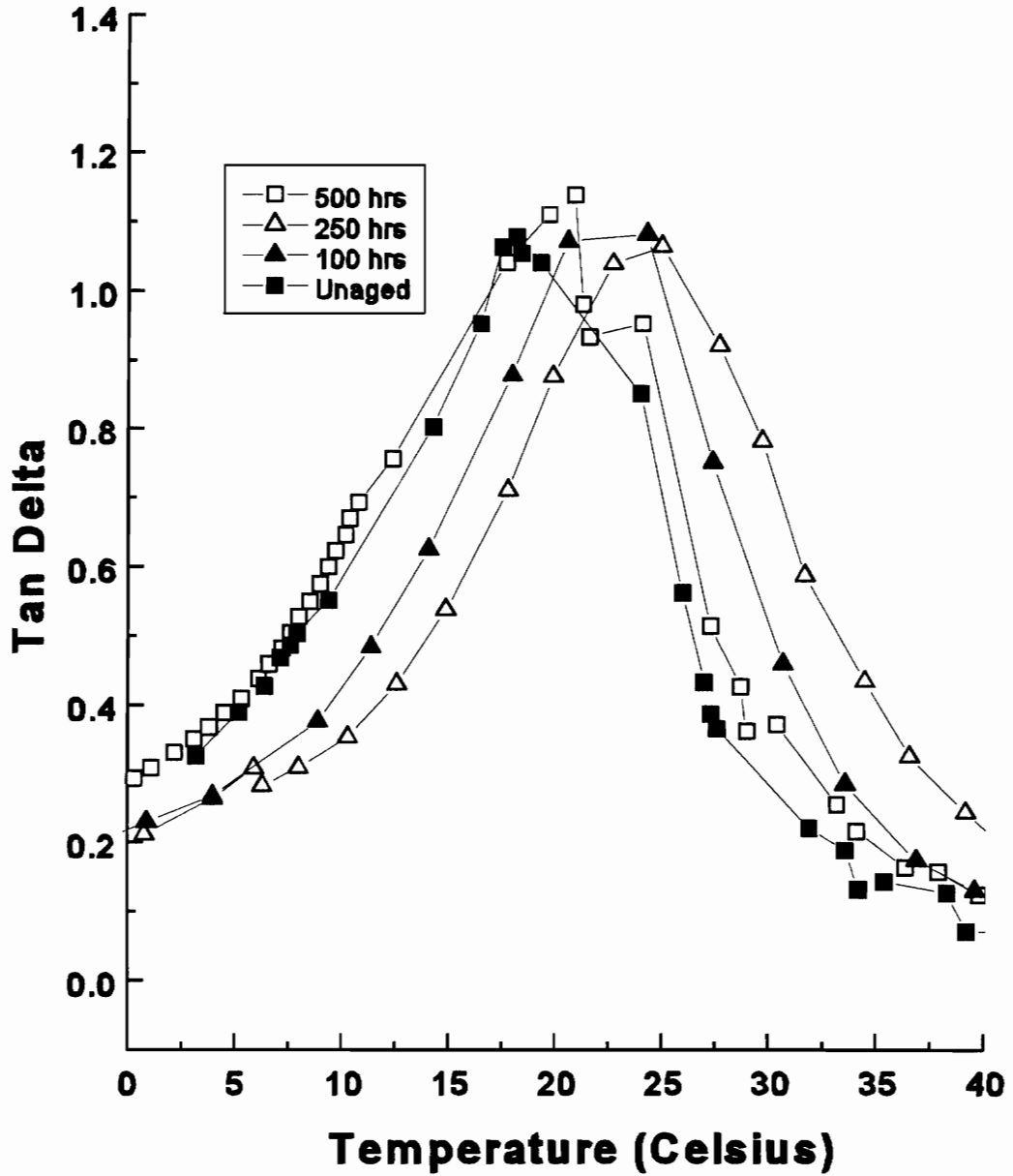
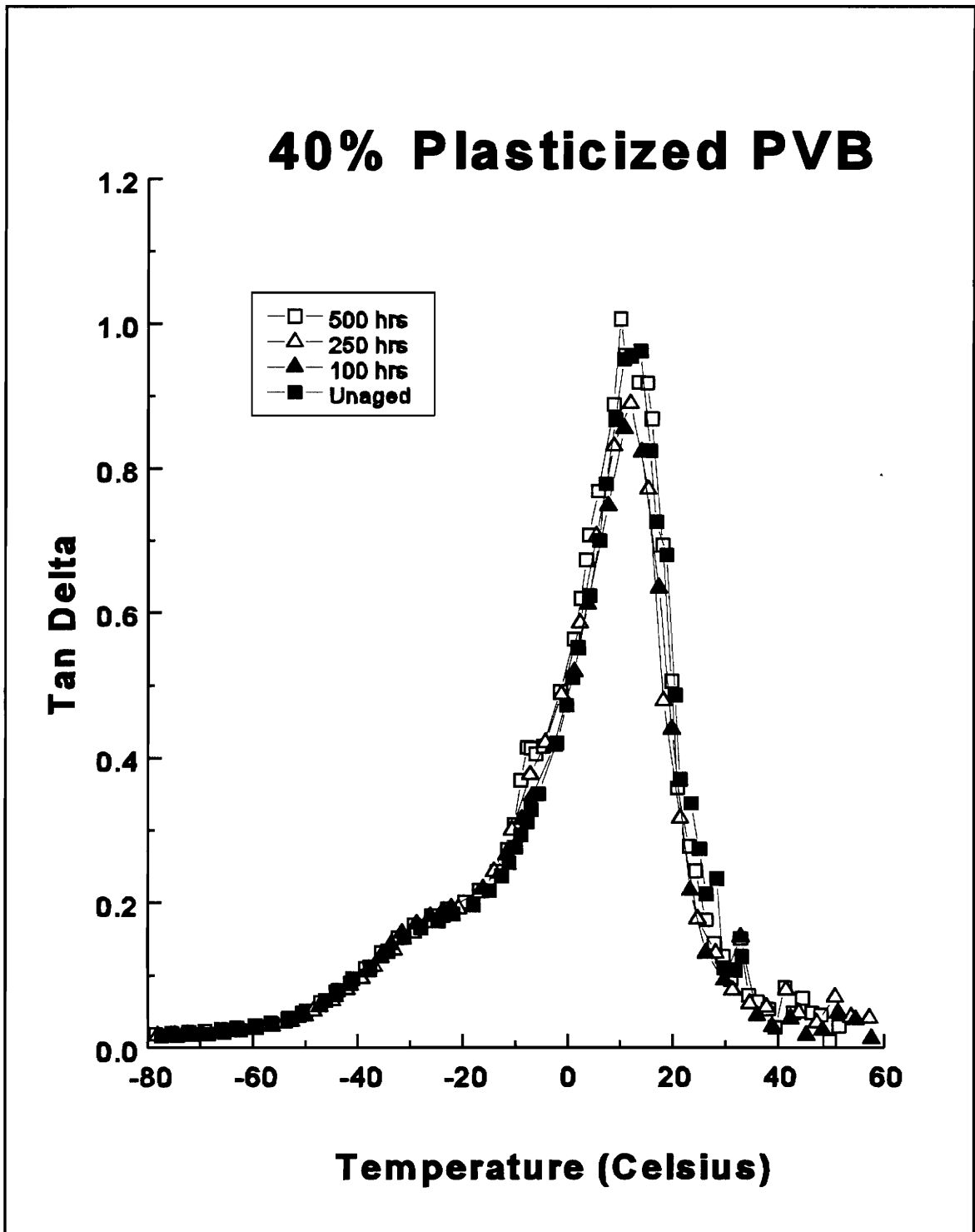
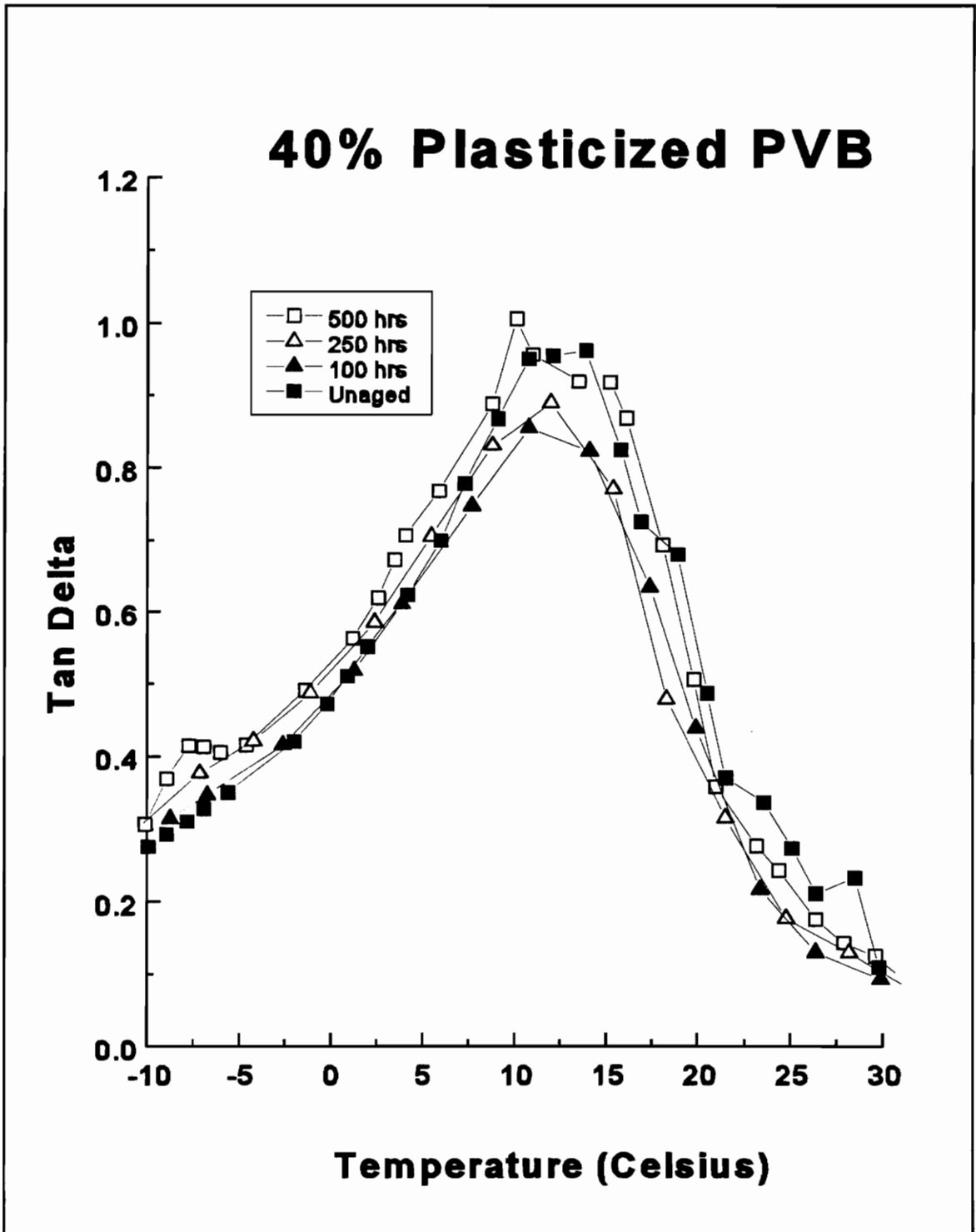


Figure 5.9. Closeup of the glass transition region in a  $\text{Tan } \delta$  plot of photoaged PVB-30.



**Figure 5.10.** Tan d plot of aged and unaged PVB-40 showing the characteristic  $\beta$  relaxation evident in heavily plasticized PVB.



**Figure 5.11.** Closeup of the glass transition region showing the absence of any observable photodegradation in the  $T_g$  of PVB-40.

## 5.2 Modulus

The room temperature mechanical properties of PVB can be broken into two categories depending on plasticizer content. For plasticizer contents equal to or less than 10%, the material acts like a typical glassy polymer. Tensile stress-strain results are presented in Figure 5.12. The neat polymer has a modulus of approximately 1100 MPa and yields at 38 MPa. After yielding, the neat polymer undergoes necking and crazing prior to failure at 110% elongation. PVB-10 behaves similarly with an initial modulus of 650 MPa and a yield stress of 24 MPa.

PVB with greater than 20% plasticizer content behaves more like an elastomeric material at room temperature. This is attributed to the continued reduction in  $T_g$  with increased plasticizer content. These materials have a glass transition temperature at or below room temperature. Tensile stress/strain curves for these materials are presented in Figure 5.13. PVB-40 has an initial modulus of 1.3 MPa increasing to a final modulus of 2.2 MPa at a break elongation of >300%. PVB-30 behaves similarly with an initial modulus of 5.5 MPa increasing to 11 MPa at a break elongation of 250 to 300%.

PVB-20 is the exception. This material has a broad  $T_g$  region which peaks between 32 and 37°C (Figure 5.7). At room temperature, the properties of this material depend heavily on the speed of the test and the amount of handling of the sample prior to testing. At low strain rates PVB-20 behaves as an elastomer slightly stiffer than PVB-30. At higher strain rates, a definite yield point is seen with post yielding behavior again

approaching elastomeric properties. Unlike the less plasticized samples, no stress release is evidenced at the yield point. At a strain rate of 10 mm/min, PVB-20 has an initial modulus of 115 MPa and a yield stress of 10 MPa.

Another means of characterizing the elastomeric, heavily plasticized formulations of PVB (PVB-20, PVB-30 and PVB-40), is the final modulus. This quantity is defined as the slope of the stress-strain curve as the material approaches failure. For each formulation, the curve approaches a linear asymptote as it elongates and the final modulus would be approximately the value of this asymptotic line. For PVB-20, the final modulus is approximately 15 MPa at a break elongation between 200 and 250%.

The differences in mechanical behavior between the samples with varying plasticizer contents is explained by the change in glass transition temperature. As plasticizer content increases, the  $T_g$  decreases, reaching the point in PVB-20 where molecular level relaxations are occurring on the same time scale as the experiment. This material has a yield point similar to PVB and PVB-10 but has elastomeric post-yield behavior signifying that relaxation is occurring within the material during the course of the experiment allowing larger elongations.

As  $T_g$  is reduced below the test temperature, the material behaves like an amorphous polymer in the leathery region. Low modulus and high elongation are the result.

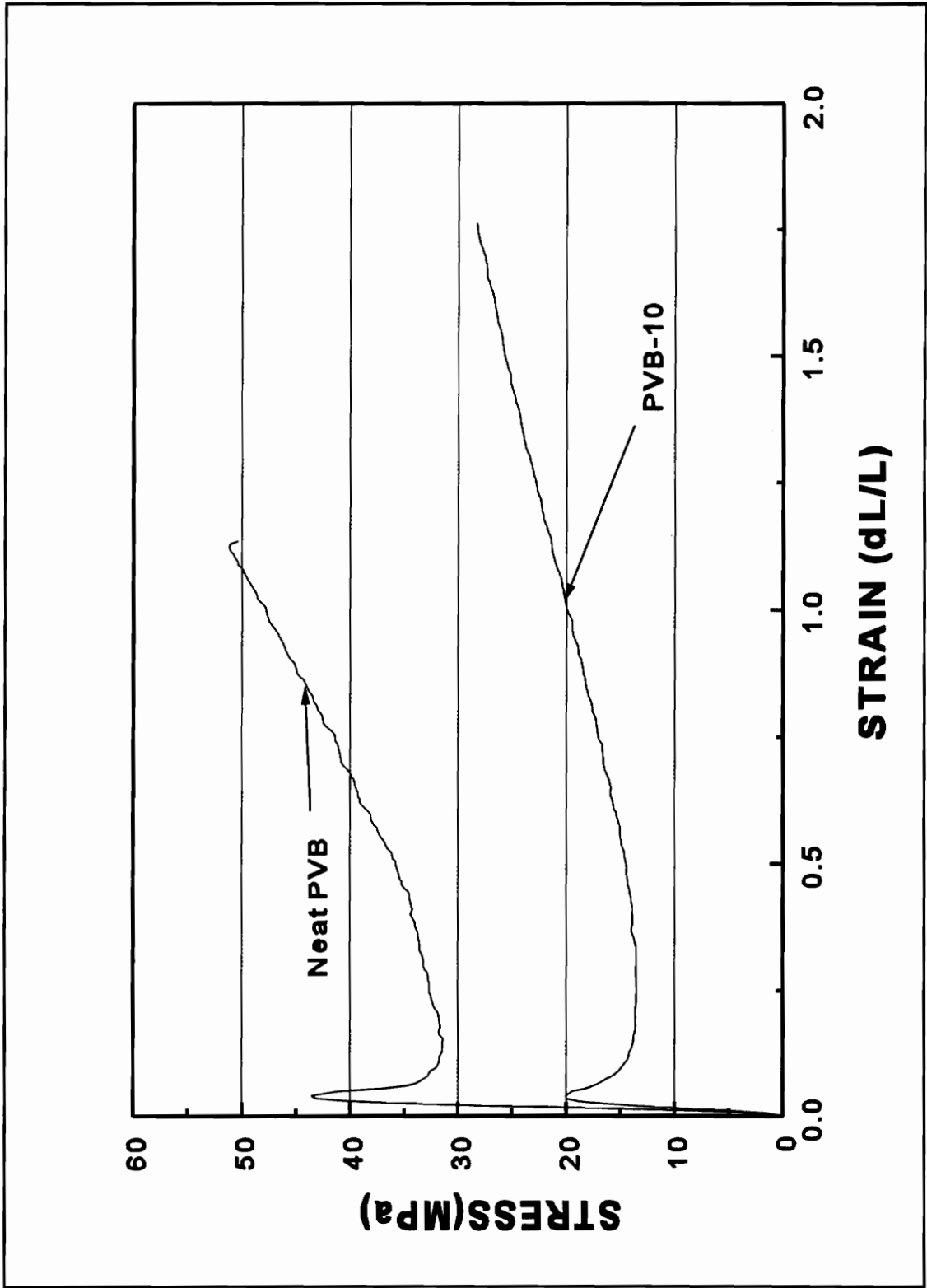
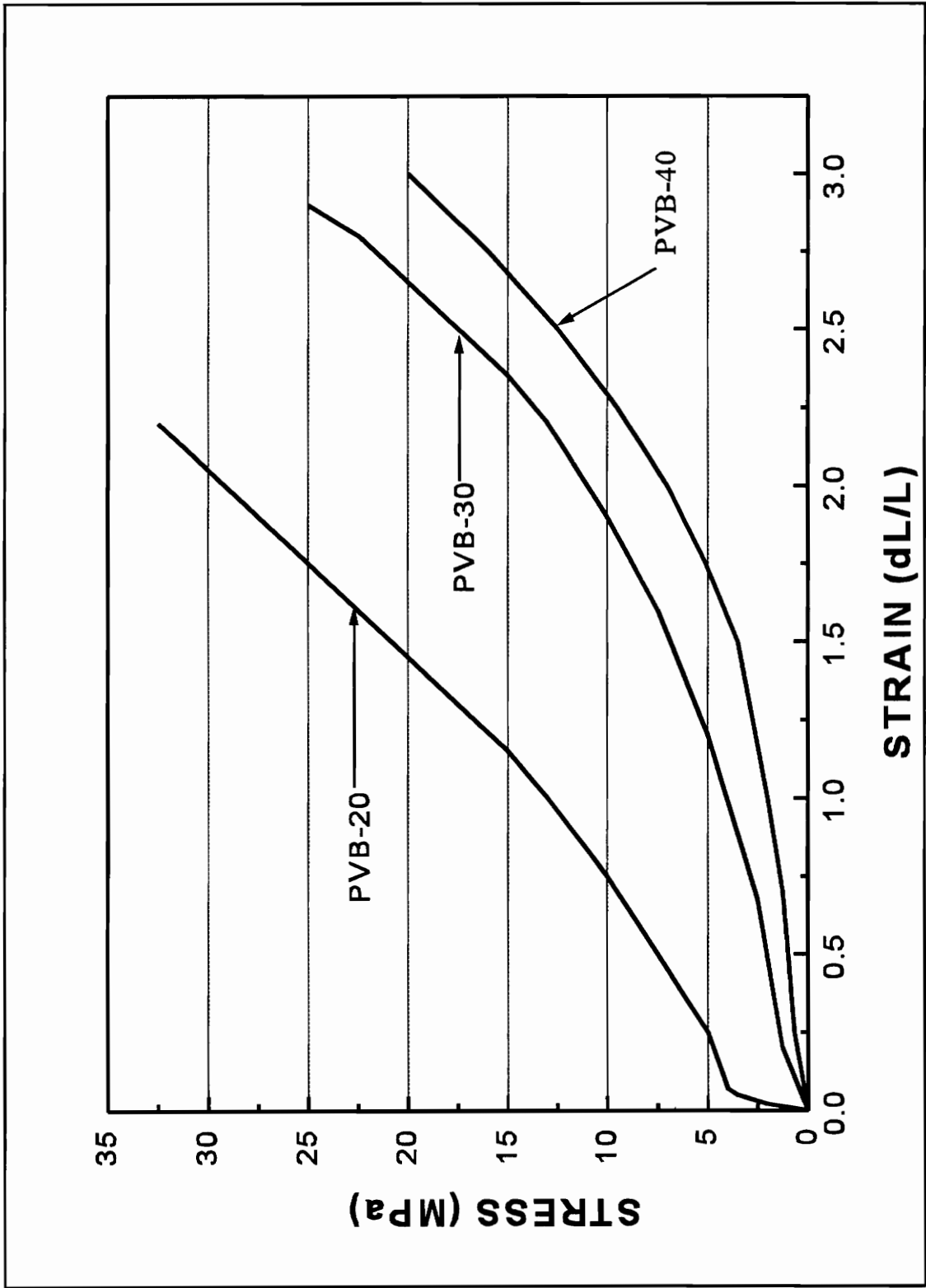


Figure 5.12. Typical tensile stress-strain curves for neat PVB and PVB-10.





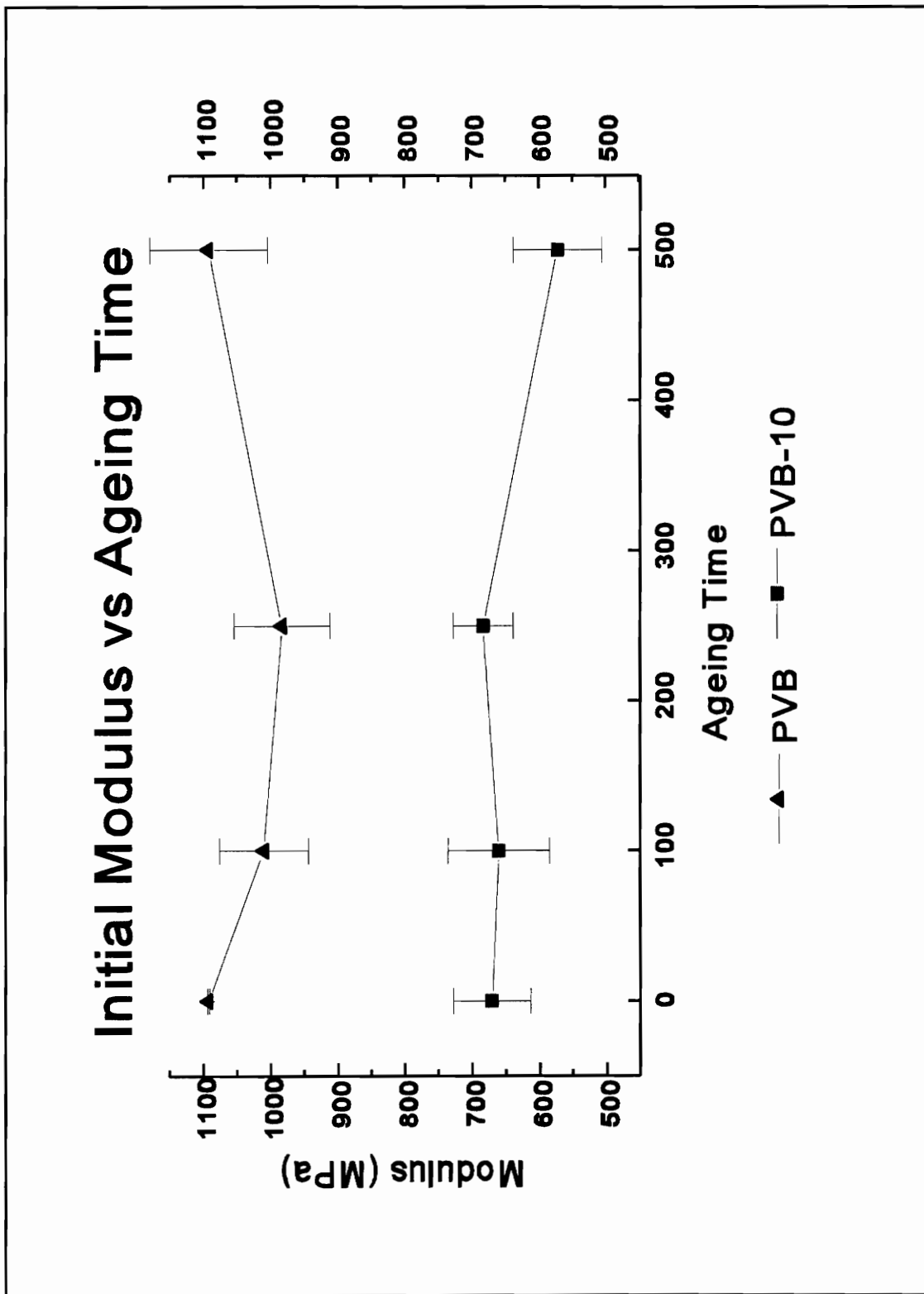
**Figure 5.13.** Typical tensile stress-strain curves for heavily plasticized PVB.

### 5.2.1 Photoageing Effects

The mechanical properties of the neat polymer have not been affected by photoageing as simulated with the R51-A lamps. Both initial modulus (Figure 5.14) and yield stress (Figure 5.15) remain relatively constant. Large variations were noticed between the samples with correspondingly high standard deviations, represented by the error bars.

Adding plasticizer affects the results slightly. The yield stress of PVB-10 decreases slightly with ageing time (Figure 5.15). An even larger decrease, approximately 10% degradation, is evidenced in the initial modulus (Figure 5.14). PVB-20 experienced a 10-15% loss in both initial modulus and yield stress after 500 hours of photoageing (Figure 5.16). Similarly, PVB-30 saw a 10% degradation in initial and final modulus (Figure 5.17). All of the above had large (>10%) standard deviations.

Increasing the plasticizer content to 40% by weight appears to reverse the trend. PVB-40 experienced no change in mechanical properties with UV exposure. Initial and final moduli are both fairly constant for the aged and unaged samples (Figure 5.18).



**Figure 5.14.** Initial Modulus of neat PVB and PVB-10 as a function of photoageing time.

# Yield Stress vs Ageing Time

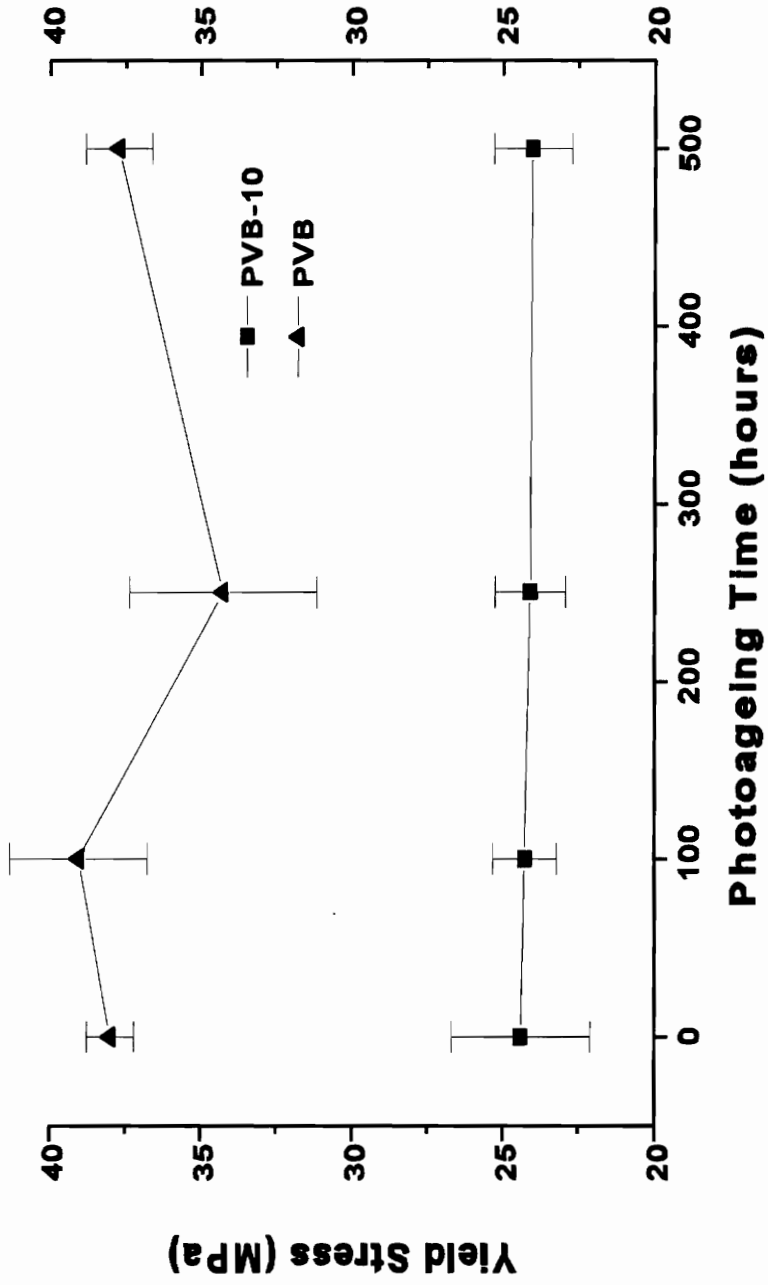


Figure 5.15. Yield Stress of neat PVB and PVB-10 as a function of photoageing time.

## 20% Plasticized PVB

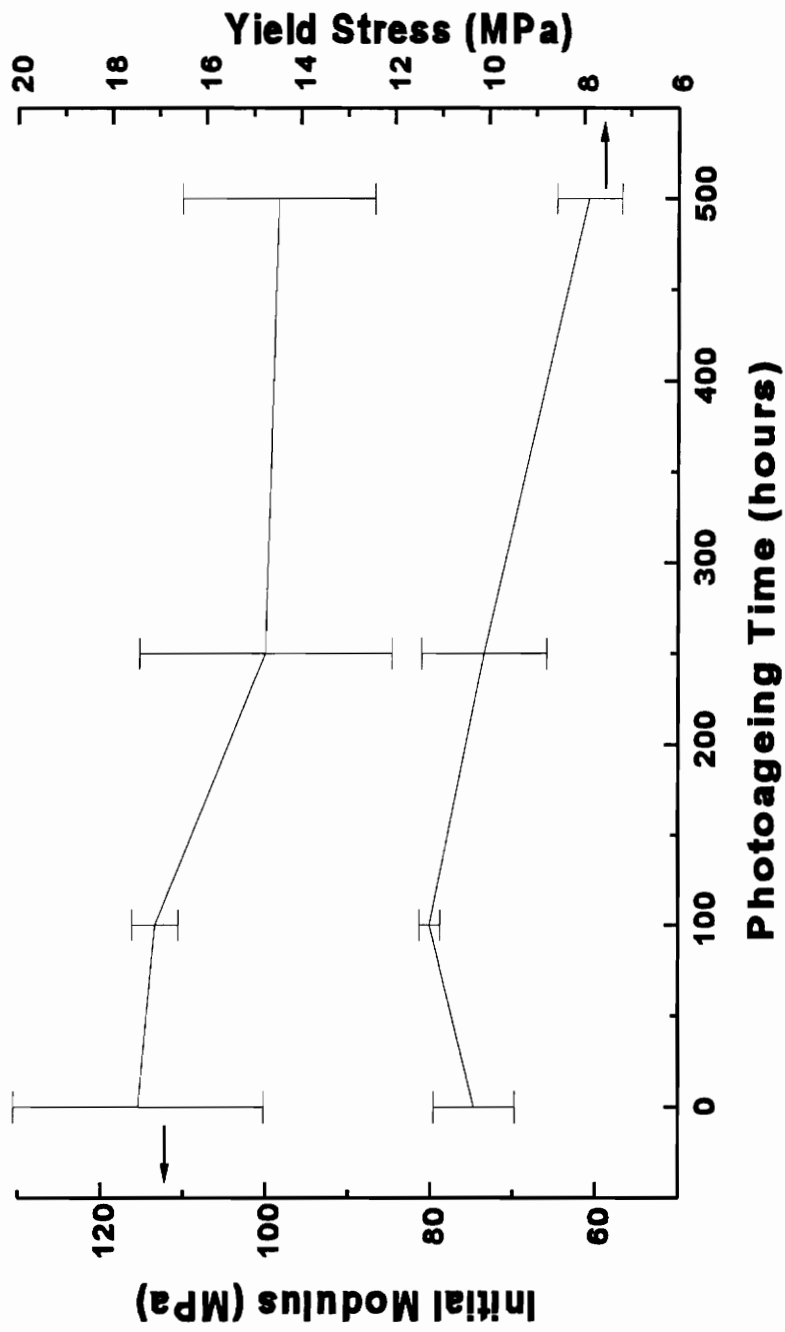
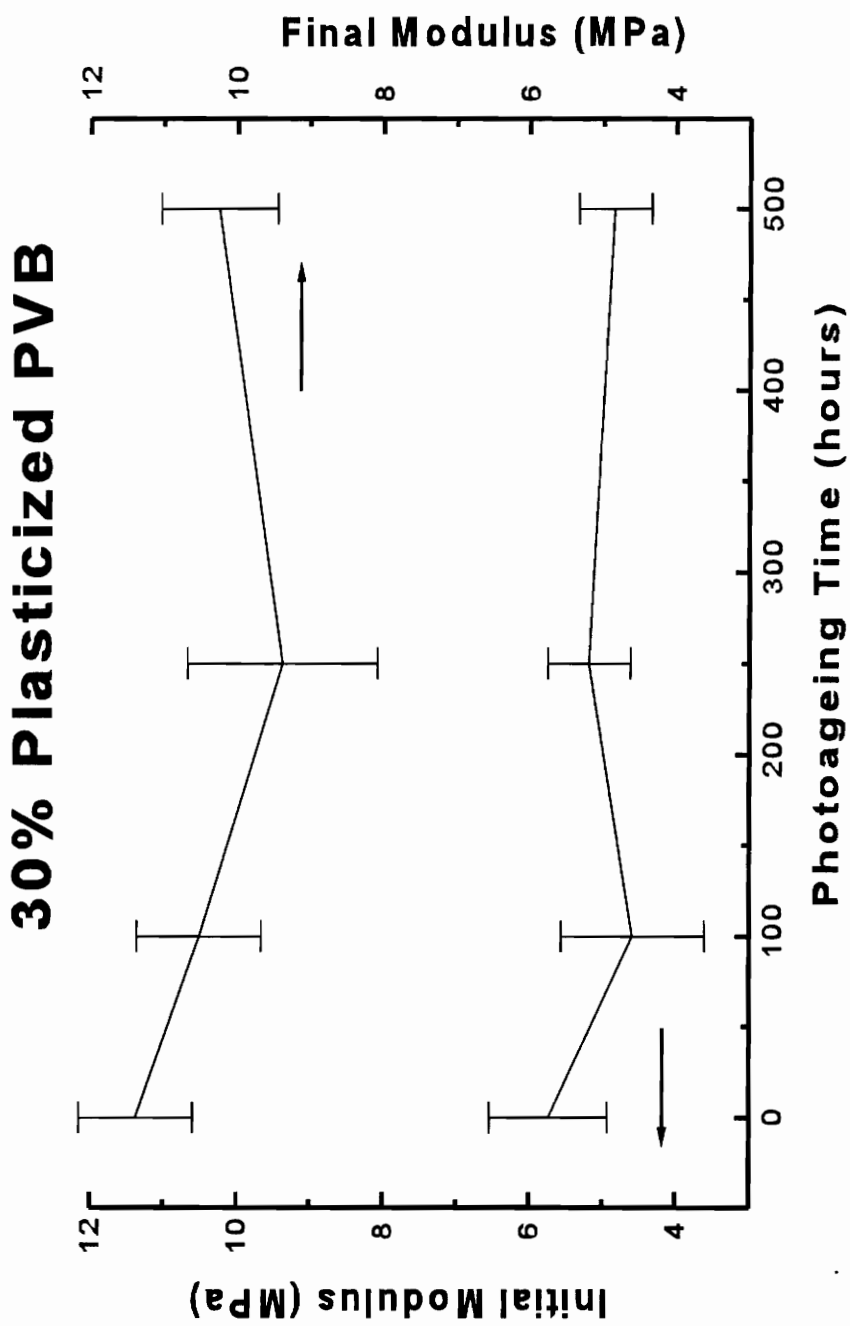
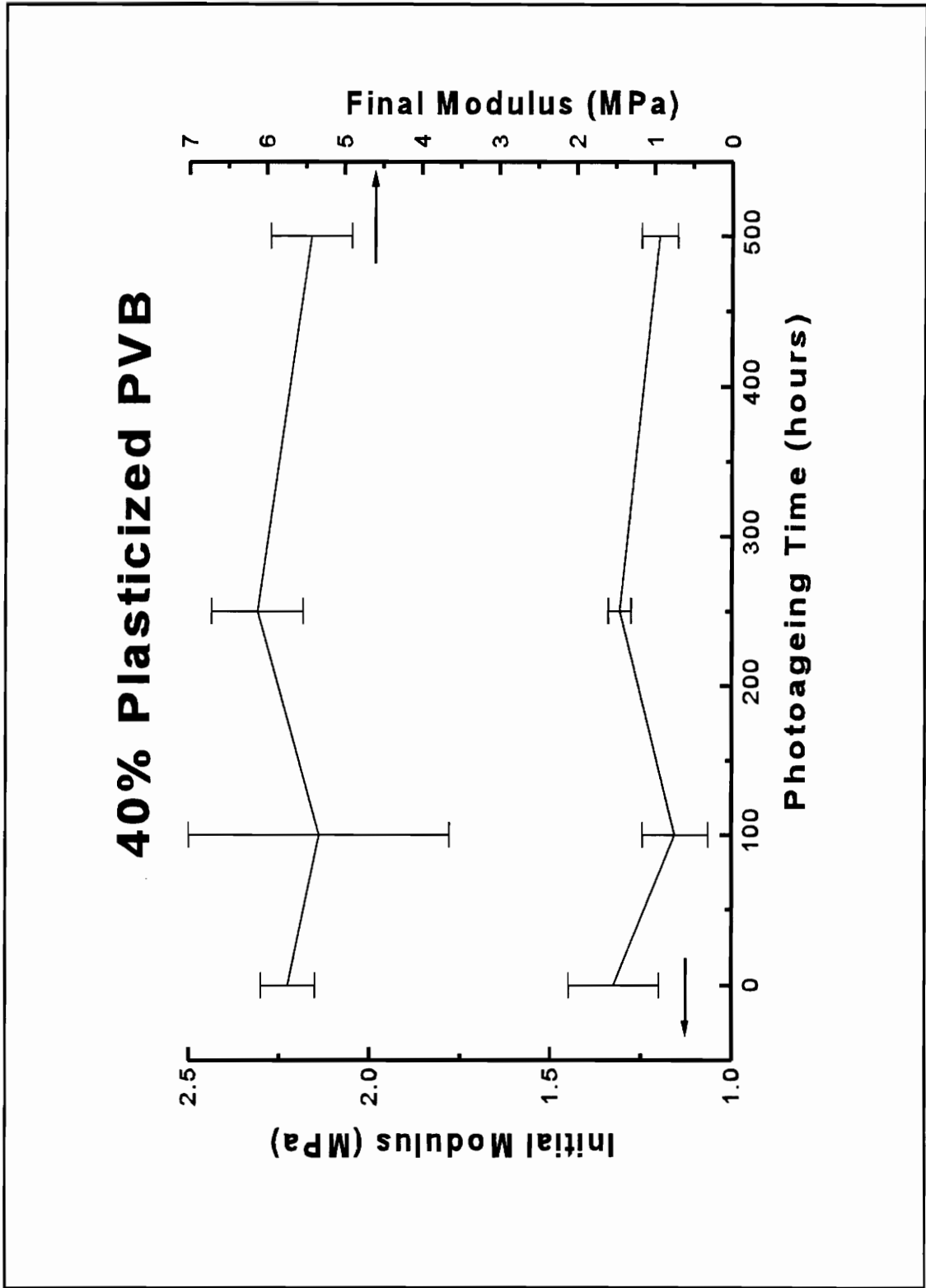


Figure 5.16. Tensile properties of PVB-20 as a function of photoaging time.



**Figure 5.17.** Tensile properties of PVB-30 as a function of photoaging time.



**Figure 5.18.** Tensile properties of PVB-40 as a function of photoaging time.

## 5.3 Discussion

The addition of plasticizer results in a decrease in  $T_g$ . This is reflected in the increased ductility of the material and a decrease in the breaking strength at room temperature. Plasticization of PVB between 20 and 40% by weight leads to an elastomeric polymer at room temperature. This allows the interlayer material to absorb the contraction and expansion of the surrounding glass layers due to changes in temperature without generating large amounts of stress.

At a plasticizer content of 40%, the  $T_g$  of the plasticized PVB broadens, extending from  $-20^{\circ}\text{C}$  to  $20^{\circ}\text{C}$  making this material particularly suited for applications where the service temperature may be below  $0^{\circ}\text{C}$ , as for example, in architectural glass. The large  $\beta$  transition found in heavily plasticized PVB is indicative of the strong impact absorption characteristics of the formulation.

### 5.3.1 Photoageing Effects

There is no apparent reason why PVB would undergo a  $20^{\circ}\text{C}$  shift in  $T_g$  with photoageing while the static mechanical properties remained unchanged. Secondly, a  $50^{\circ}\text{C}$   $T_g$  is low for unplasticized PVB. Therefore, the result must be due to experimental error, either residual trapped solvent or an improperly run DMTA experiment. The  $T_g$  of neat PVB sold by Monsanto has a published value of  $72-74^{\circ}\text{C}$  which agrees well with the aged samples.



The apparent degradation in the mechanical properties of PVB-20 and PVB-30 is not reflected in the DMTA results. PVB-20 shows little or no effect in either  $T_g$  or the  $\beta$  transition with exposure time. The  $T_g$  of PVB-30 shifts to higher temperatures which is the exact opposite of the expected trend. With the evidence of the mechanical degradation, the  $T_g$  should decrease.

Conversely, the DMTA results for PVB-40 correlate well with the tensile tests performed. No change in  $T_g$  results in no observed change in the mechanical properties as a function of UV exposure.

Taken together, the results from both the static and dynamic mechanical tests performed do not reflect the photodegradation discovered using FTIR. The breakdown of the acetal ring structure should reduce the mechanical stiffness. This would be offset to an unknown degree by a rise in  $T_g$  if crosslinks formed as suggested by previous research. However, there was no evidence of the formation of crosslinks in either the mechanical or spectroscopic samples. The samples remained soluble in THF after photoageing. Decreases in moduli were only evidenced in PVB-10, -20 and -30 and the decrease was small, within the standard deviation of the results.

These results suggest that the amount of radical formation is small relative to the number of chains in the sample. It is possible that the strength of the UV light decreased between the time of photoageing the FTIR samples and the ageing of the mechanical samples.

The lack of degradation evidenced in the mechanical property measurements may also be explained by the difference in thickness between the two types of samples. The FTIR samples were a maximum of .08 mm thick, roughly ten times thinner than the mechanical samples. Assuming a linear relationship between thickness and energy absorbed per chain, the mechanical samples exposed for 500 hours would correspond to FTIR samples aged for only 50 hours. The FTIR samples exposed to 100 hrs of radiation show only a slight increase in the carbonyl peak. Therefore, it is entirely reasonable that the mechanical property measurements would reveal little degradation.

The lack of agreement of these results with previously published research suggests that the level of UV exposure in this study was significantly lower than used in previous studies. Unfortunately, none of these exposure levels have been compared to actual levels present in normal sunlight and thus it is difficult to correlate the results of these ageing experiments with the in use conditions of safety glass.

## VI. ADHESION TESTING

### 6.1 Peel Testing

Neat and plasticized PVB/glass test pieces were each peeled at a number of different temperatures and loadings. Samples of PVB-40 were initially peeled at an angle of 45°C. Each of these samples failed cohesively away from the interface regardless of the load applied. Samples, again of PVB-40, were then peeled at an angle of 135°C. These failed at or near the interface with no apparent stretching of the unbonded sections. For this reason, the rest of the specimens were tested at the larger peel angle.

From these tests a relationship between  $G$ , the strain energy release rate, and the crack growth rate,  $\dot{a}$ , can be determined. The variance of  $G$  with crack growth rate is typically modeled as a power law function:

$$G = k \cdot \dot{a}^n$$

such that on a log-log plot the data will appear as a straight line. This model was used to represent the adhesion of both neat and plasticized PVB to a glass substrate.

The data from the tests performed on unaged neat PVB are presented in figure 6.1. The points fall on a straight line for a given isotherm. The tests performed at 70°C are offset to higher crack growth rates for a given loading from the data at 60°C. The experiments were performed at lower temperatures but the transitional behavior of the

polymer led to dramatically varying behavior ranging from stick-slip crack growth to catastrophic growth. To limit the failure mode to adhesive and/or cohesive near the surface, the rest of the samples were tested at 60°C or above. Similarly, high temperature testing > 75°C led to cohesive failure of the sample. Thus, to measure interfacial failure in a controlled fashion, temperatures were kept between 60°C and 75°C for neat PVB.

The peel results from the plasticized PVB/glass are similar to the neat PVB/glass and are presented in figures 6.2 thru 6.5. The temperature range was again limited to the region around  $T_g$ ,  $T_g-10^\circ\text{C}$  to  $T_g+10^\circ\text{C}$ . The large, leathery transition region present in PVB-40 allowed testing at temperatures as much as 30°C above  $T_g$ . Unfortunately, the lack of any cooling mechanism in the test equipment precluded testing PVB-30 or PVB-40 at their given  $T_g$ .

By testing at various temperatures it is possible to develop master curves spanning a broader range of crack growth rates at a given temperature than can be reasonably tested. The method of time-temperature superposition was used to generate the master curves found in figures 6.6 through 6.10. The line drawn through the points is the linear regression curve fit of the data after shifting. The shift factors were generated by maximizing the  $r^2$  fit of this line. Values of  $r^2$  ranged from a low of .839 for the neat polymer to a high of .967 for PVB-30. Each of the curves was shifted to the lowest temperature at which the material was tested. The linear fit of each material is replotted

in figure 6.11. This technique allows comparison of the material at their relative  $T_g$ 's over a broad range of crack growth rates from  $10^{-7}$  to  $10^{-3}$  m/sec.

The log shift factors for PVB-10 and PVB-40 fall roughly on a straight line suggesting that time-temperature superposition is valid for plasticized PVB (Figure 6.12 and 6.13). (Note: There was insufficient data for the other formulations to comment on the shape of their shift factor plots.) From this data an apparent activation energy of 570 kJ/mol (130 kcal/mol) for PVB-10 was calculated. Similarly, PVB-40 was determined to have an apparent activation energy of 130 kJ/mol (30 kcal/mol). These are reasonable values for the secondary relaxations which govern the time-temperature codependence of the bond strength of plasticized PVB/glass constructions.

PVB-30 and PVB-40 behave very similarly at room temperature (21 °C). At this temperature, PVB-20 requires significantly more energy to debond at the same crack growth rate. This is probably due to PVB-20 being at or slightly below its glass transition, whereas PVB-30 and PVB-40 are slightly above their respective  $T_g$ 's. PVB-10 at 45 °C requires similar amounts of energy for a given rate as PVB-20, diverging slightly as the rate decreases, for the same reason that 45°C is approximately 10°C below the  $T_g$  of PVB-10. The curve for neat PVB falls in the middle of the range.

From these results, the peel strength of PVB-30 and PVB-40 are expected to be comparable or possibly even greater than that of PVB-10 or PVB-20 when measured at their lower  $T_g$ 's. By comparing the different grades at their respective  $T_g$ 's, the degree of

energy dissipation within the material is maximized overshadowing any differences in bond strengths.

Comparing the three commercial grades, PVB-20, -30 and -40, at room temperature it is readily apparent that PVB-20 has the highest bond strength. Stated differently, PVB-20 absorbs the most energy when debonded from glass.

The use of time-temperature superposition and a broad range of test temperatures and loading rates has allowed the comparison of measured bond strength at a common point for each formulation, that of the glass transition temperature. The close agreement between the values obtained for PVB-10 and PVB-20 suggest that the same bonding mechanism is responsible for the adhesive strength of a glass/PVB bond and that the differences between the samples tested at the same temperature are attributable to the differences in energy absorption characteristics within the material itself. Unfortunately, the inability to test at sub-ambient conditions means that a comparison could not be drawn between PVB-30 and PVB-40 and the other grades at their respective  $T_g$ .

The addition of plasticizer to PVB increases the room temperature peel strength. This can be attributed to an increase in the energy absorption ability of the bulk polymer as the test temperature approaches the glass transition region. Twenty degrees below  $T_g$ , the adhesion between PVB and glass becomes very low as demonstrated by neat PVB and PVB-10 which had little or no peel strength at room temperature. As the chain mobility increases with temperatures approaching  $T_g$ , the adhesion strength improves.

For this reason, PVB-20, -30 and -40 have measurable adhesive strength at room temperature. Assuming the same behavior for all of the formulations, PVB-40 will retain significant adhesive strength even at sub-ambient conditions.





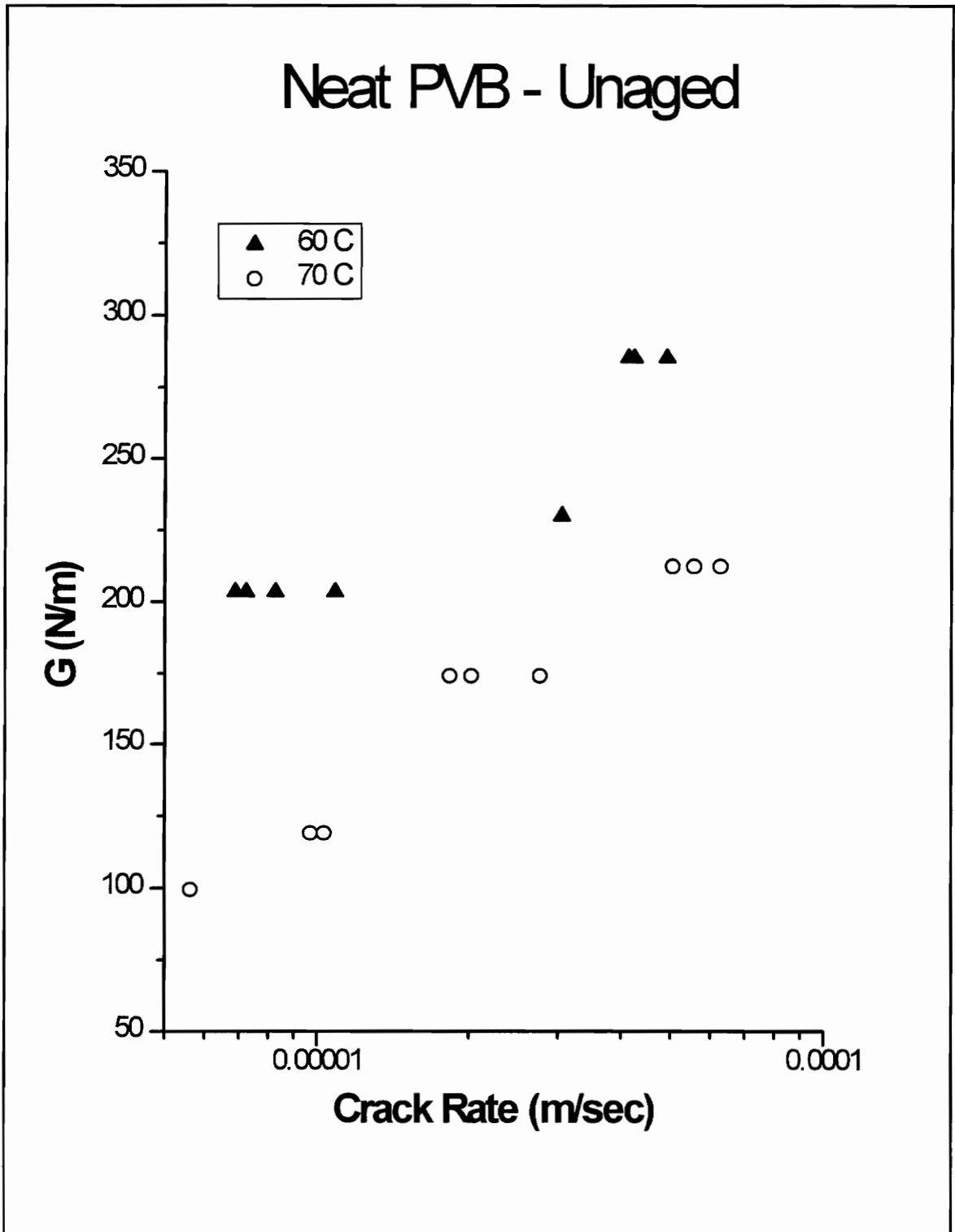
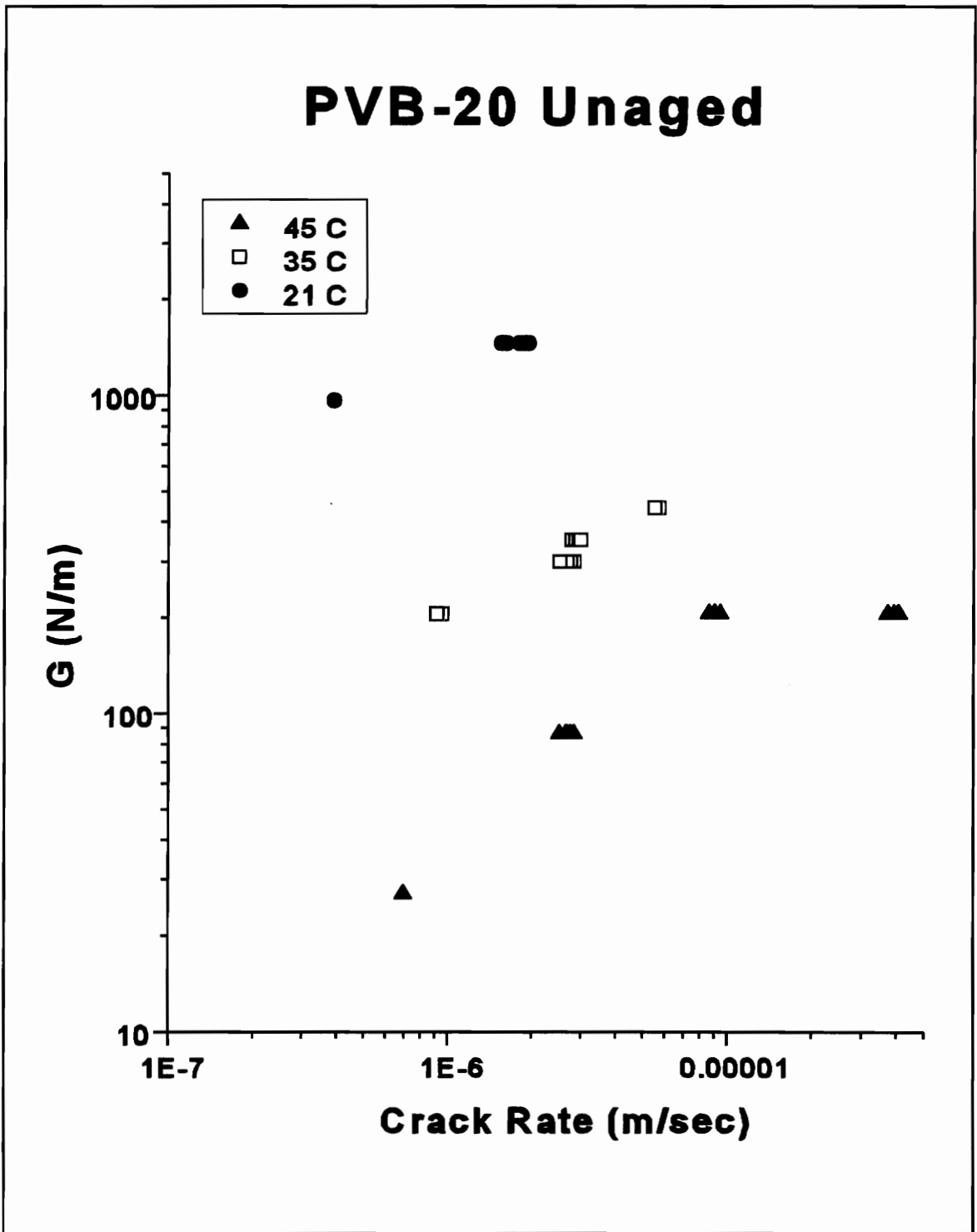
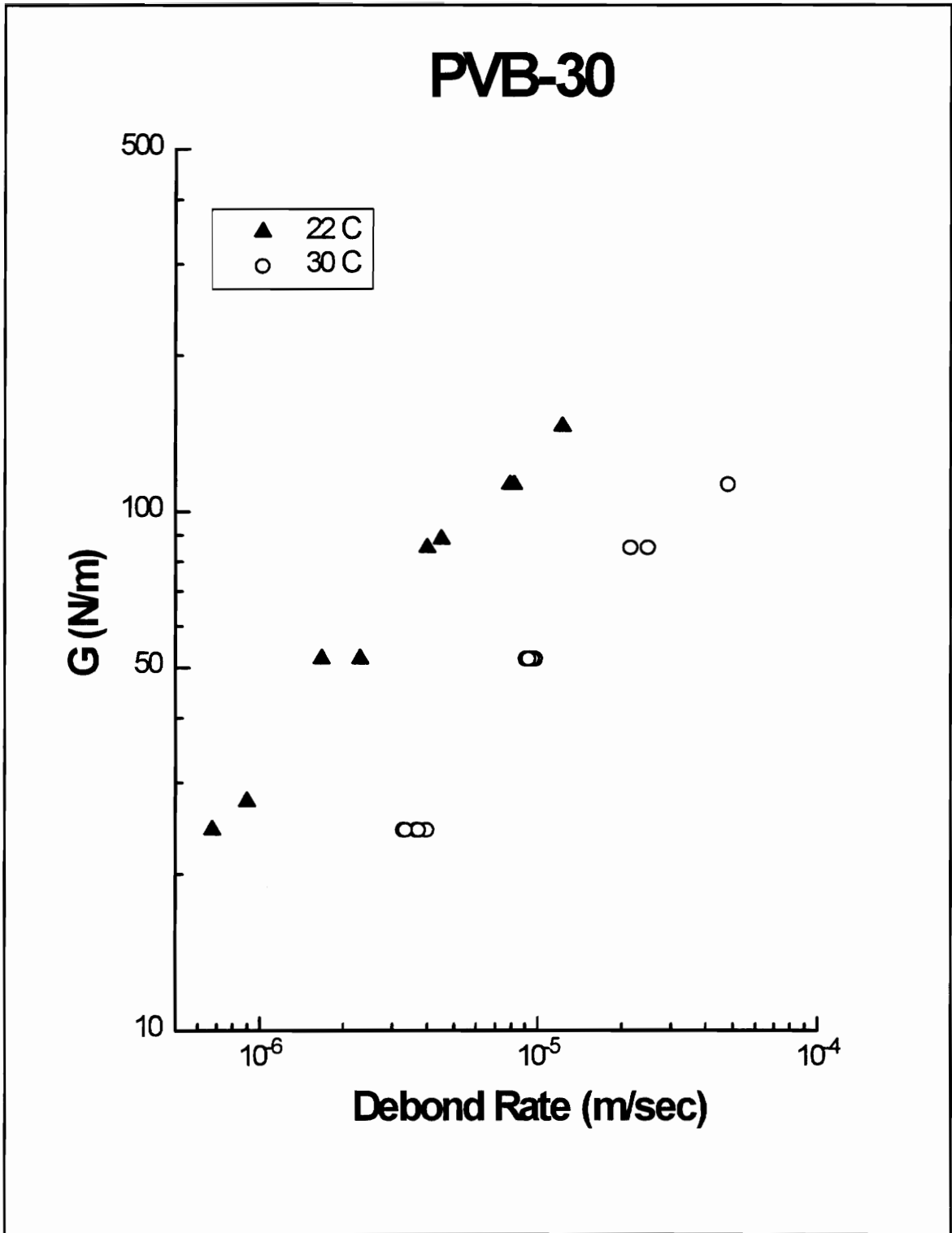


Figure 6.1. Peel data for neat PVB tested at two different temperatures.

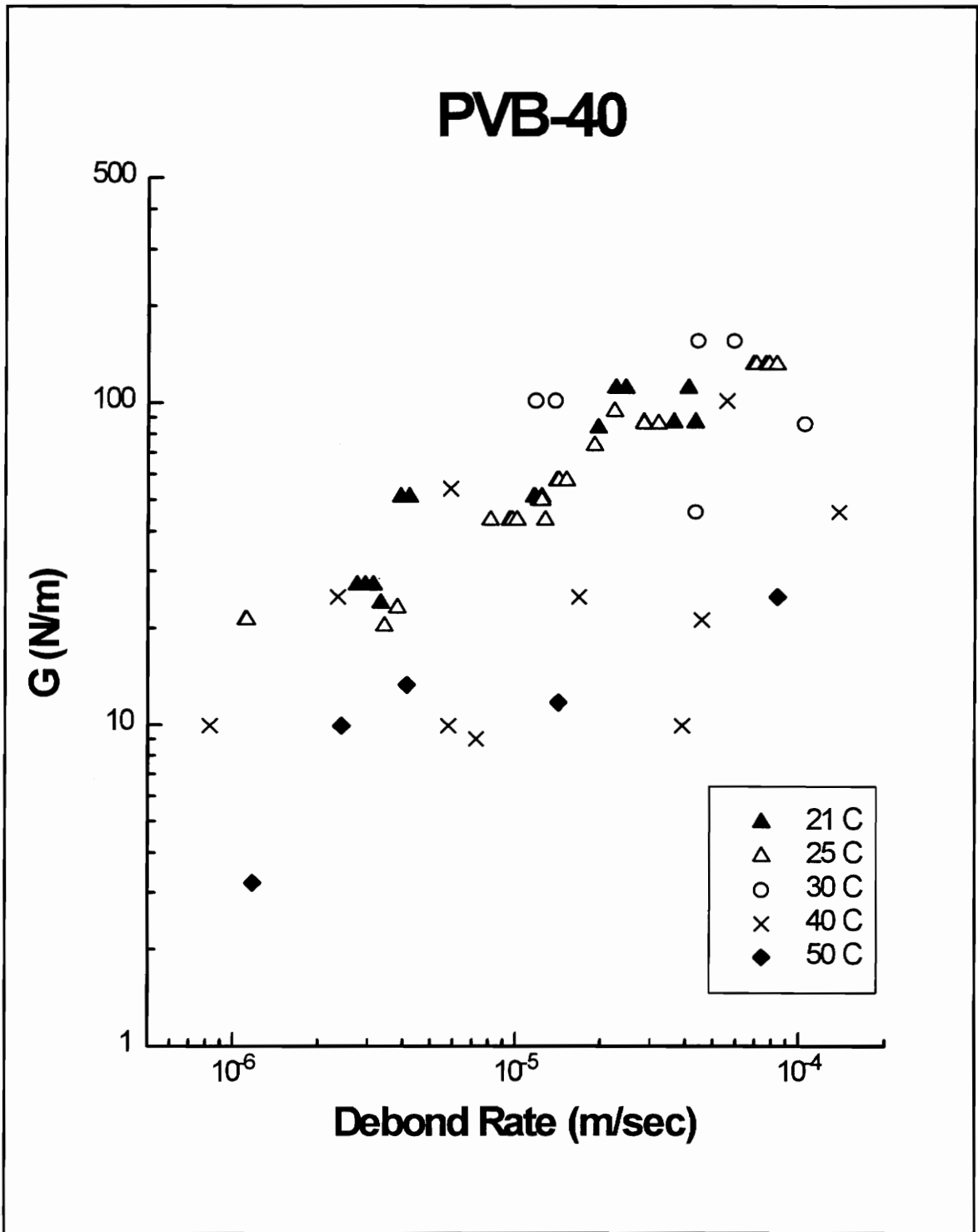




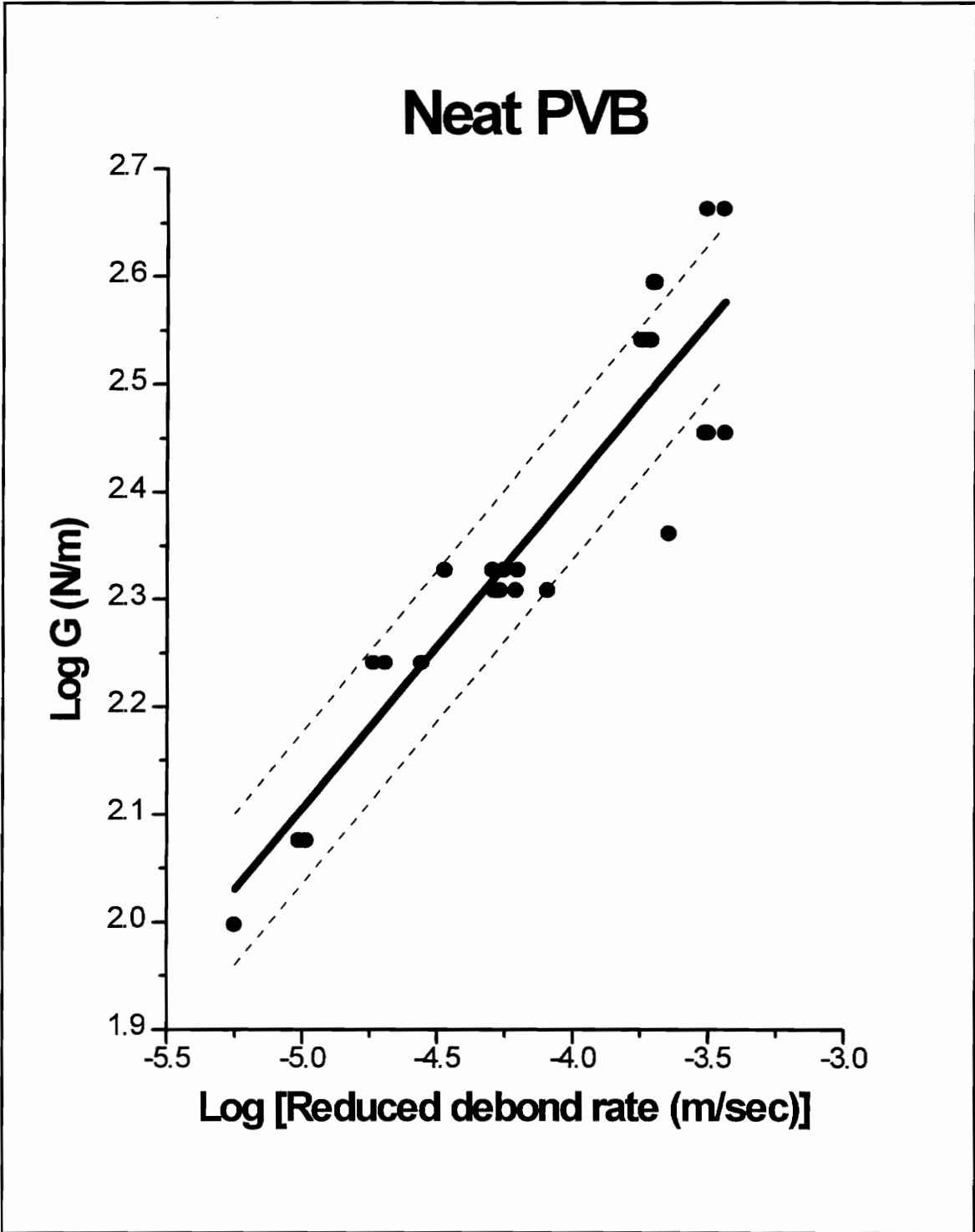
**Figure 6.3.** Peel data for PVB-20 tested at temperatures ranging from room temperature to 45°C.



**Figure 6.4.** Peel data for PVB-30 at room temperature and 30°C.



**Figure 6.5.** Peel data for PVB-40 tested at temperatures ranging from room temperature to 50°C.



**Figure 6.6.** Peel master curve of Neat PVB shifted to 70°C. The dotted lines represent the standard error of the reduced debond rate.

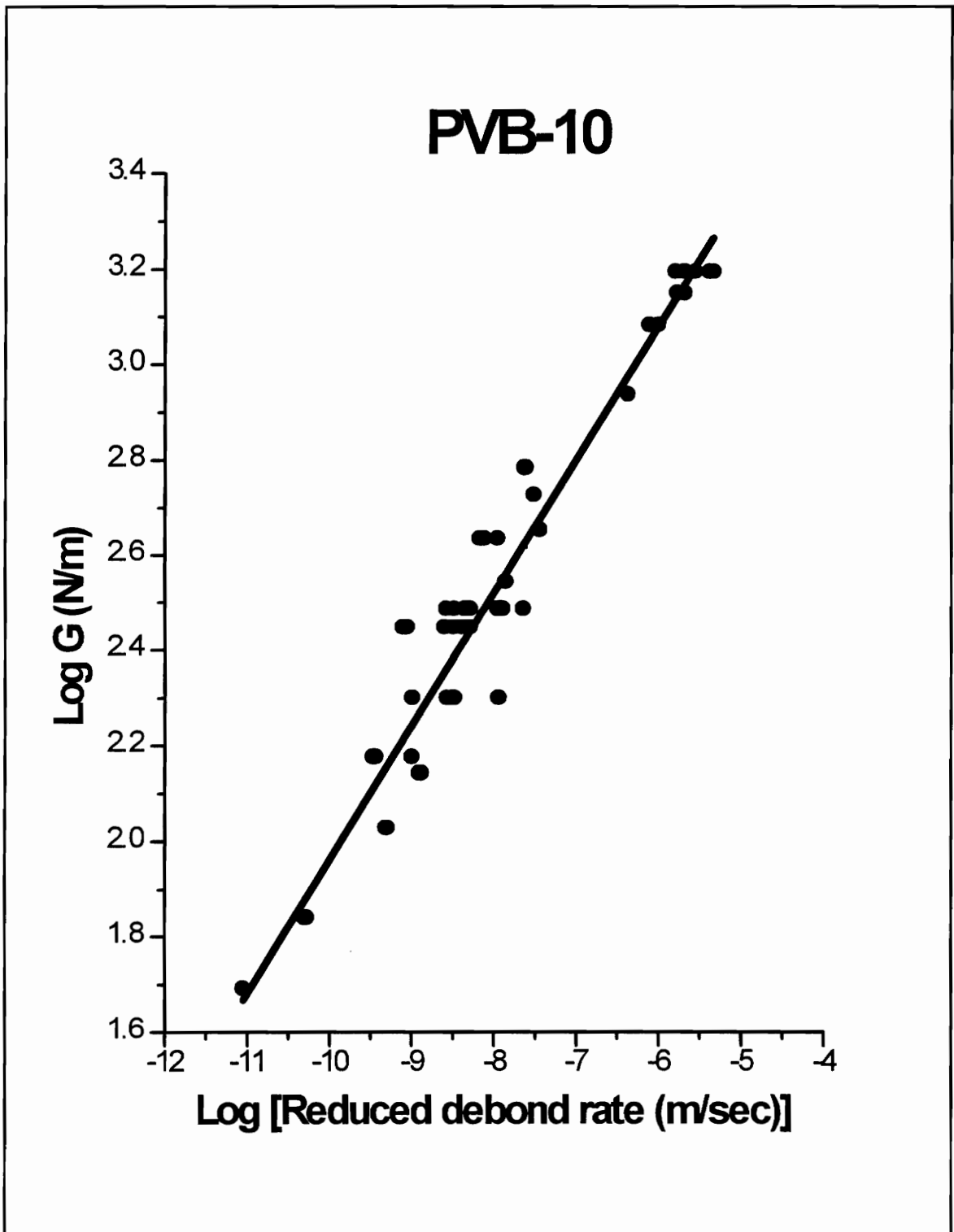
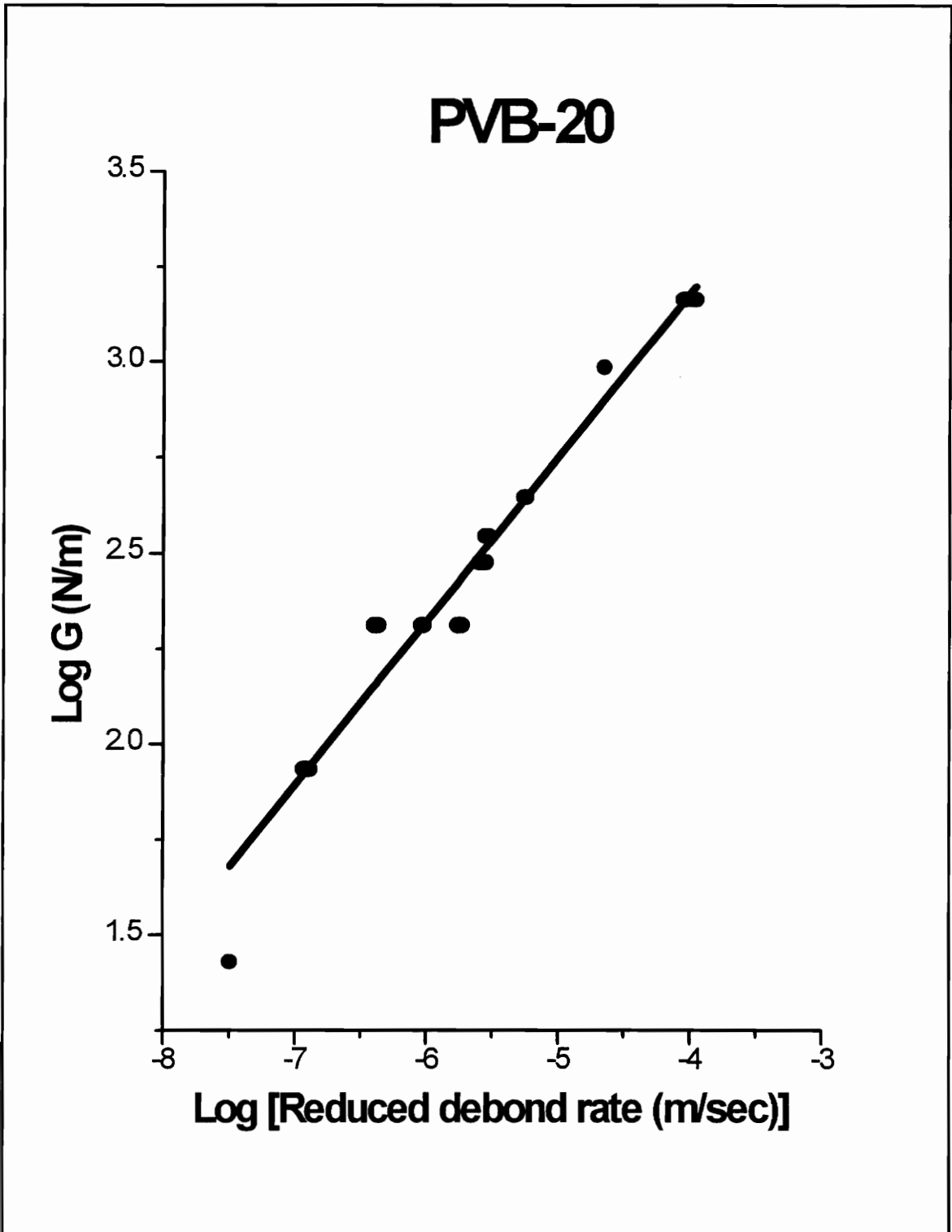
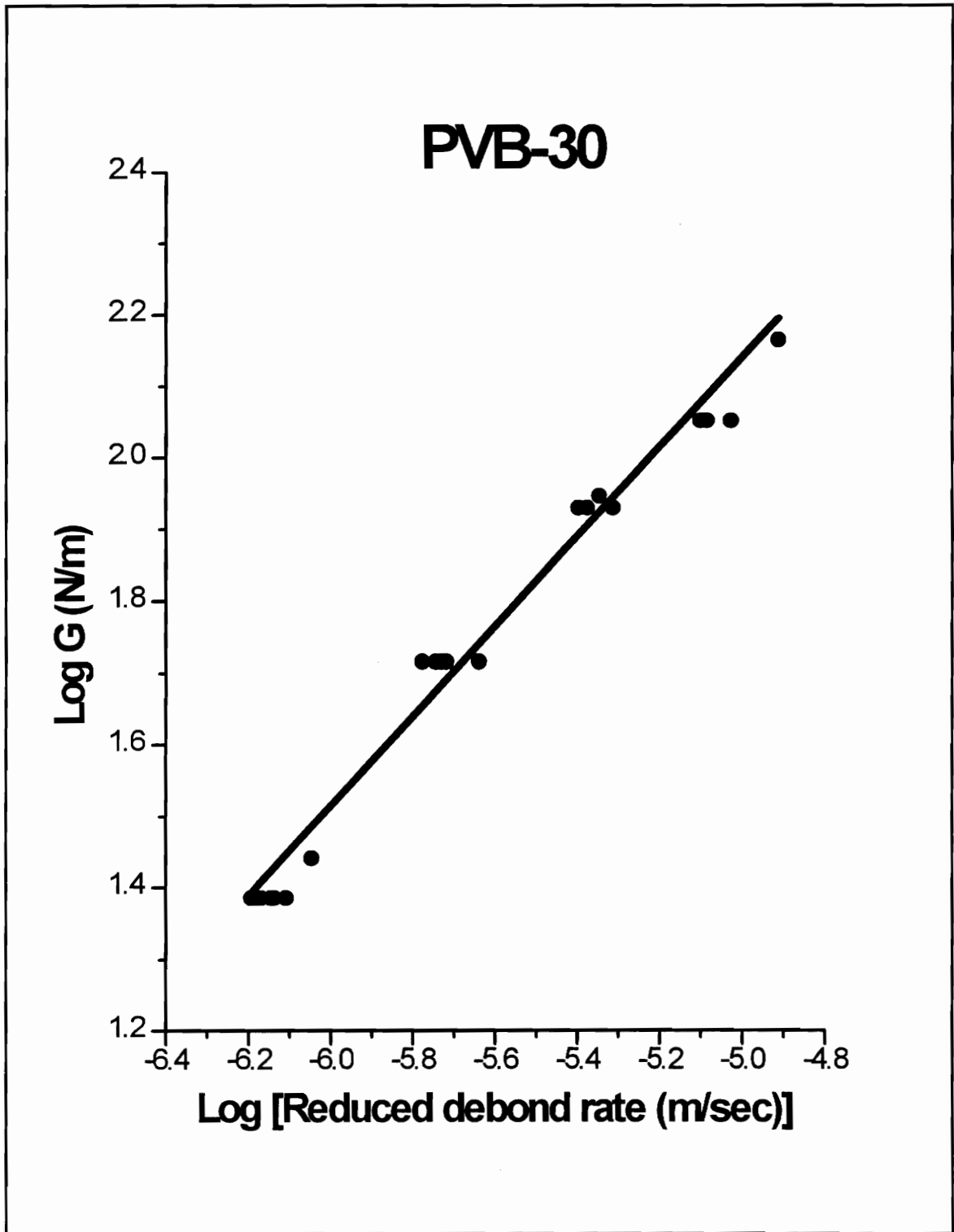


Figure 6.7. Peel master curve of PVB-10 shifted to 45°C.

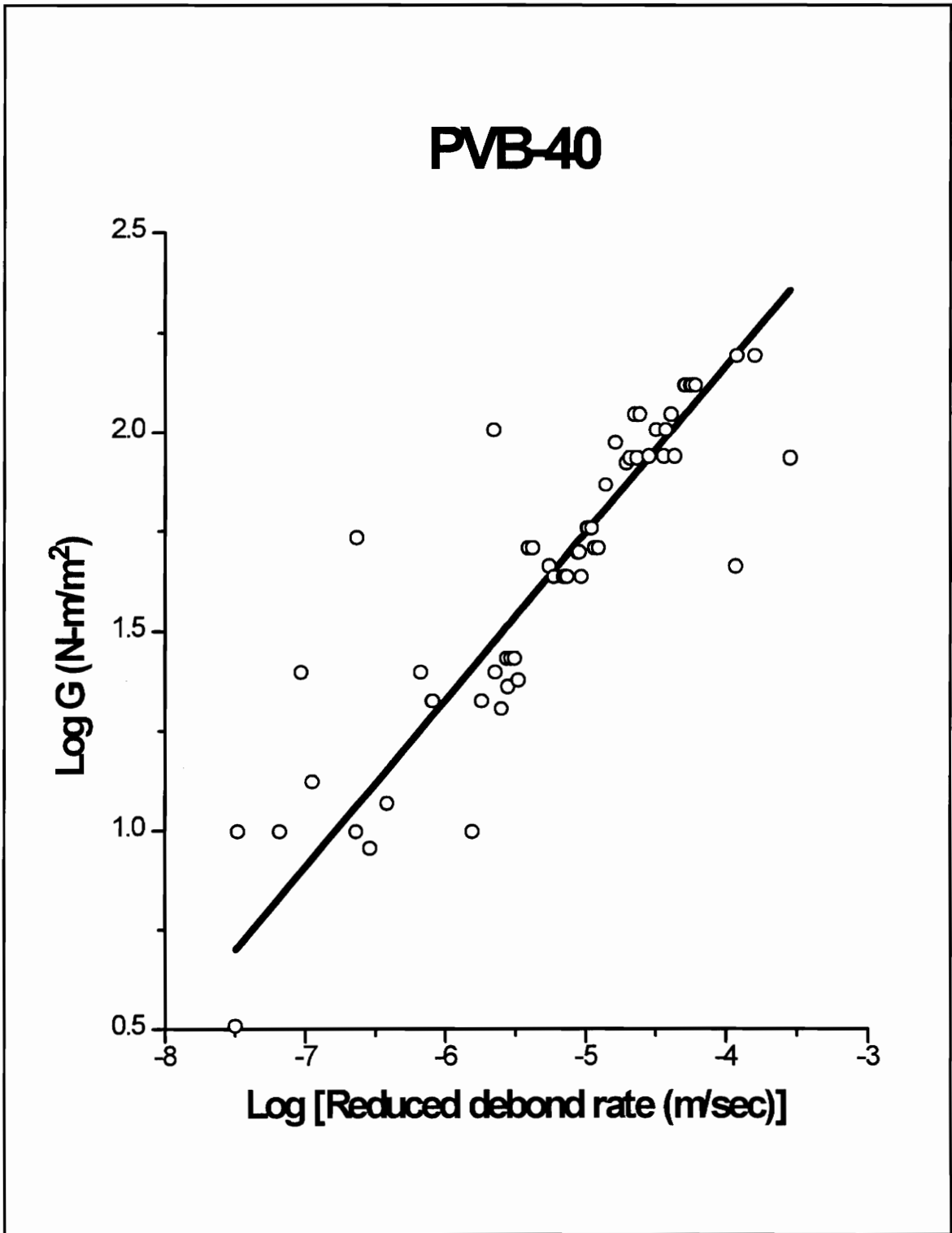


**Figure 6.8.** Peel master curve of PVB-20 shifted to 35°C.

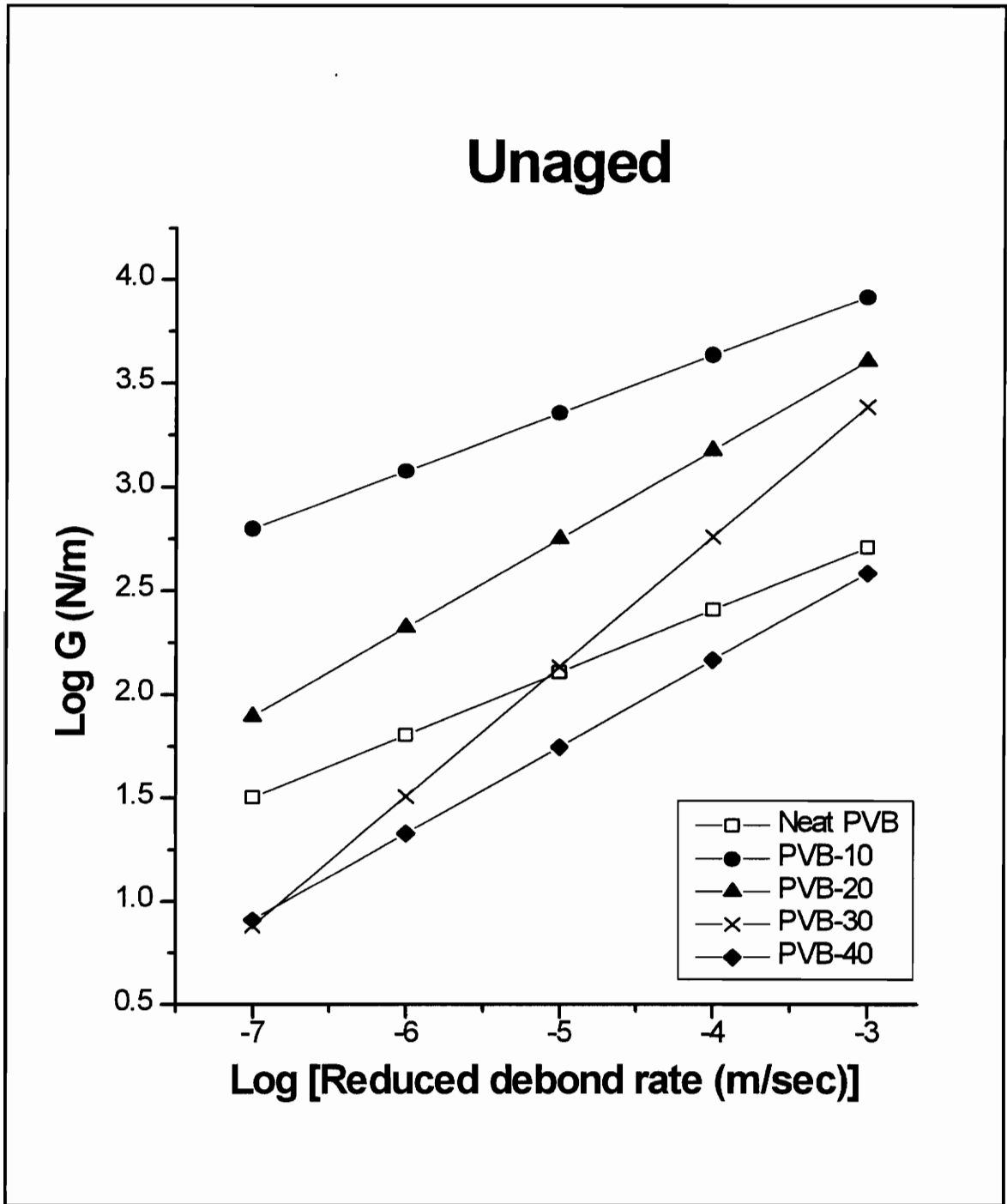




**Figure 6.9.** Peel master curve of PVB-30 shifted to room temperature.



**Figure 6.10.** Peel master curve of PVB-40 shifted to room temperature.



**Figure 6.11.** Visual comparison of the peel master curves for each of the formulations shifted to their respective glass transition temperatures. (\*Note: PVB-30 and PVB-40 peel master curves were shifted to room temperature (23°C) since this was the lowest temperature at which tests were performed.

# PVB-10

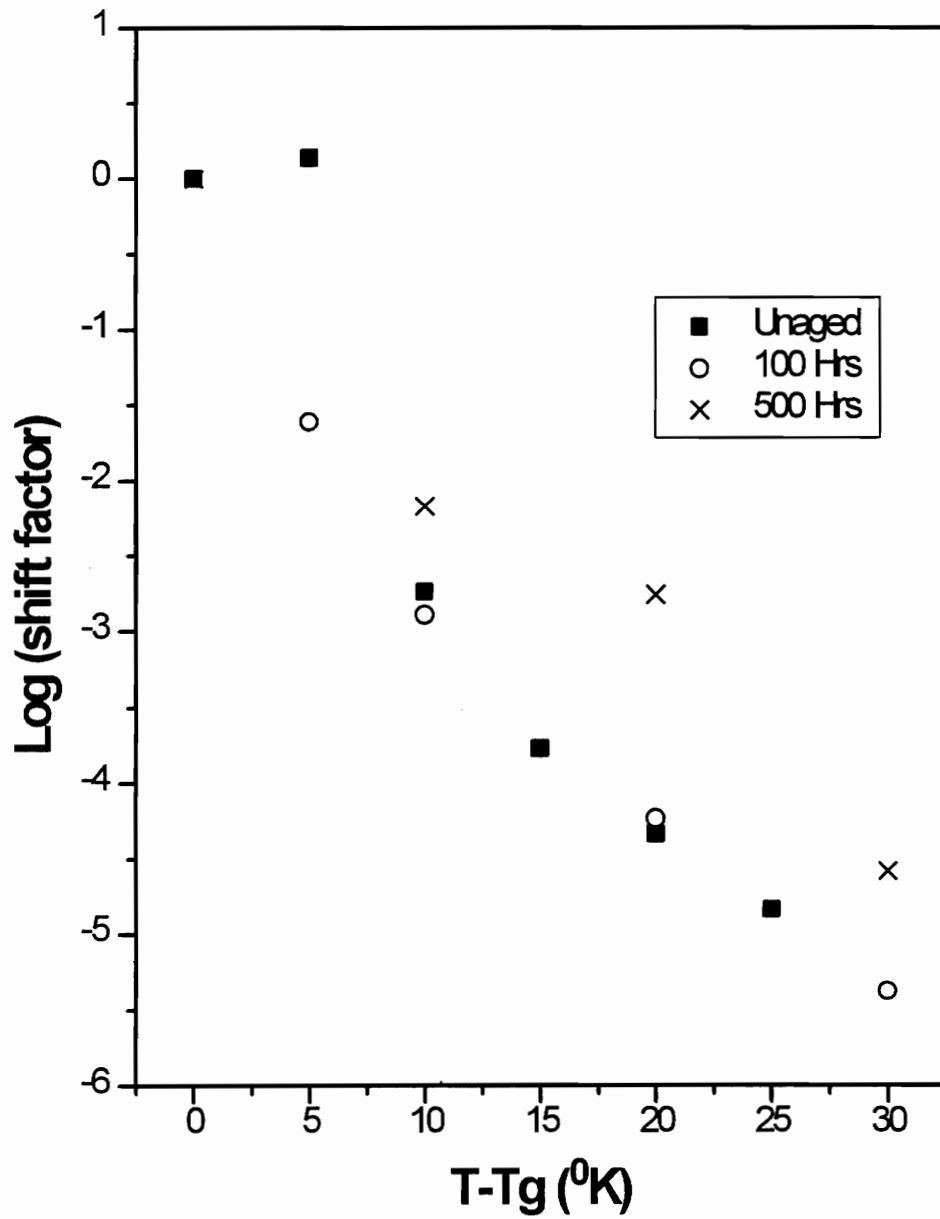


Figure 6.12. Shift master plot for PVB-10.

# PVB-40

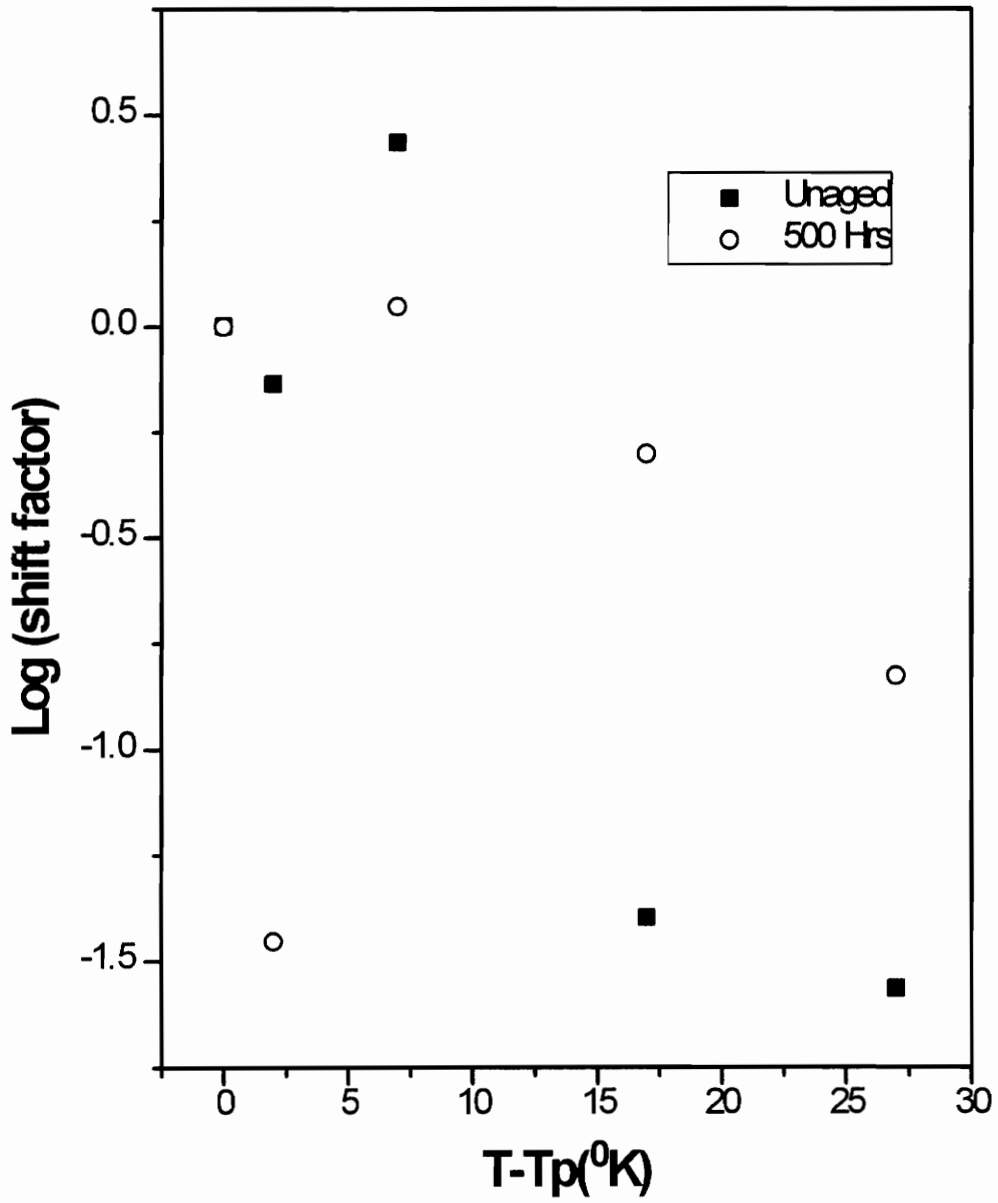


Figure 6.13. Shift master plot of PVB-40.

### 6.1.1 Photoageing Effects

Samples from each of the grades were photoaged up to 500 hours and then tested in the same fashion as the unaged sample. Time-temperature superposition was again used to generate master curves for each of the materials at a given ageing. The results are presented in figures 6.14 through 6.18.

Photoageing increases the peel strength of neat PVB/glass constructions.(Figure 6.14) The unaged sample has the lowest peel strength which increase for each of the exposure times. Photoageing has the opposite effect on PVB-10.(figure 6.15) The unaged sample has the highest strength at the slow crack speeds although the curves converge as the crack growth rate increases.

PVB-40 behaves similarly to neat PVB with the unaged sample having less strength than that of the sample exposed for 500 hr.(figure 6.18) The results are not as clear for PVB-20 and PVB-30.(figure 6.16 & 6.17) For PVB-20, the unaged sample appears to have the highest strength with the 500 hr sample competing with the 100 hr sample for lowest strength. PVB-30 has the highest strength after 250 hrs, with the unaged sample falling in the middle. The first 3 ageing times, 0-250 hrs, all converge to the same G as the crack growth rate increases. The 500 hour sample again has the lowest strength over the range of crack growth rates.

# Neat PVB

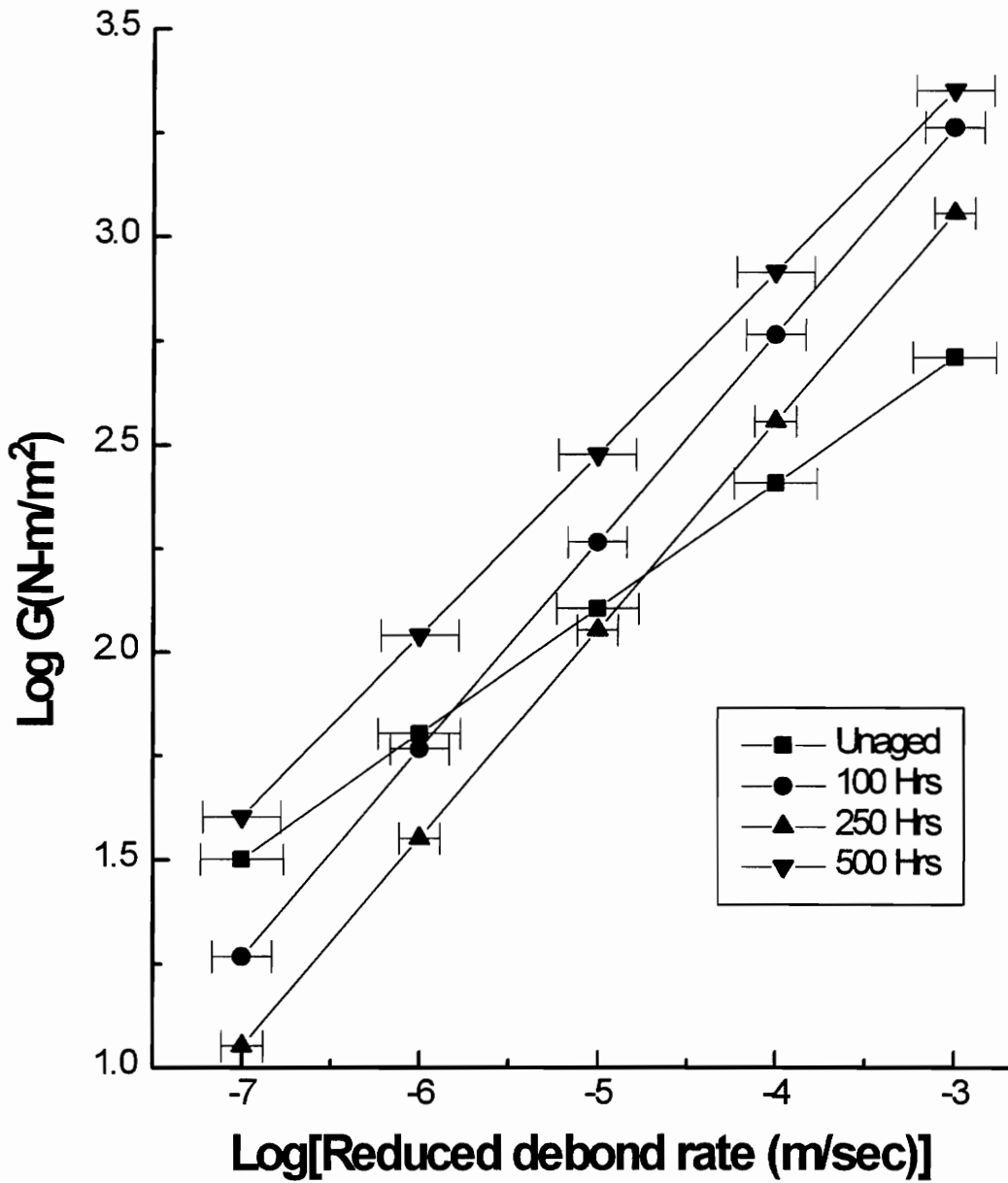


Figure 6.14. Peel master curves for photoaged neat PVB.

# PVB-10

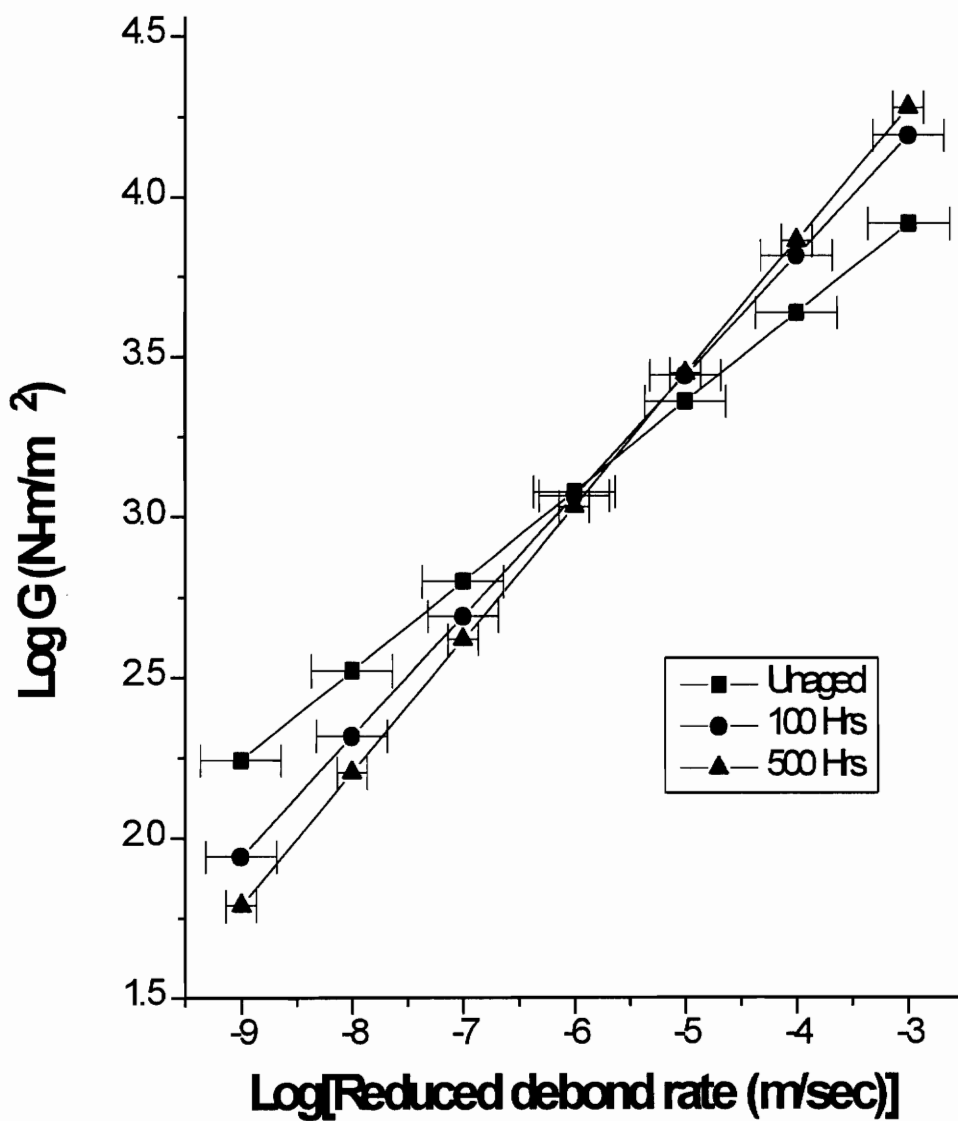


Figure 6.15. Peel master curves for photoaged PVB-10.



# PVB-20

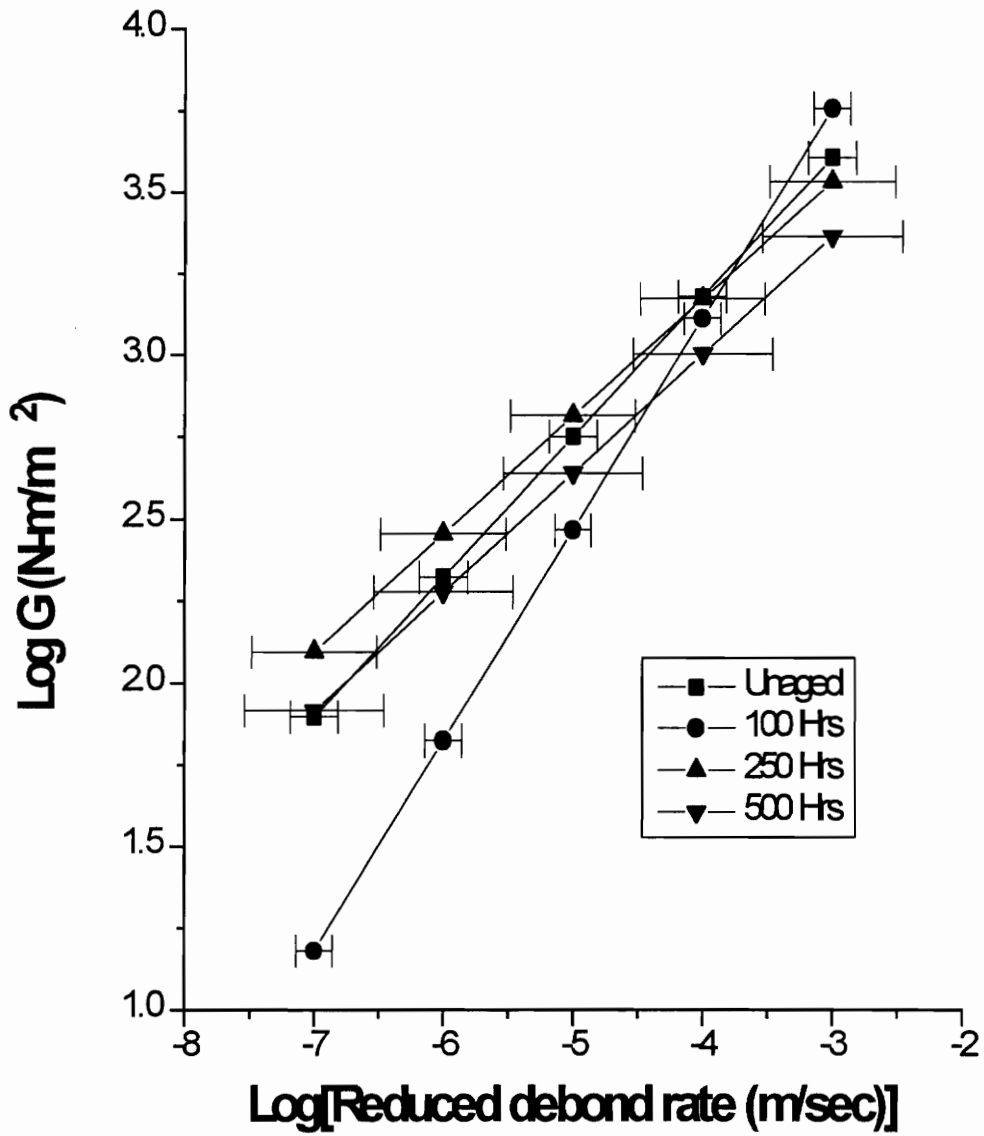


Figure 6.16. Peel master curves for photoaged PVB-20.

# PVB-30

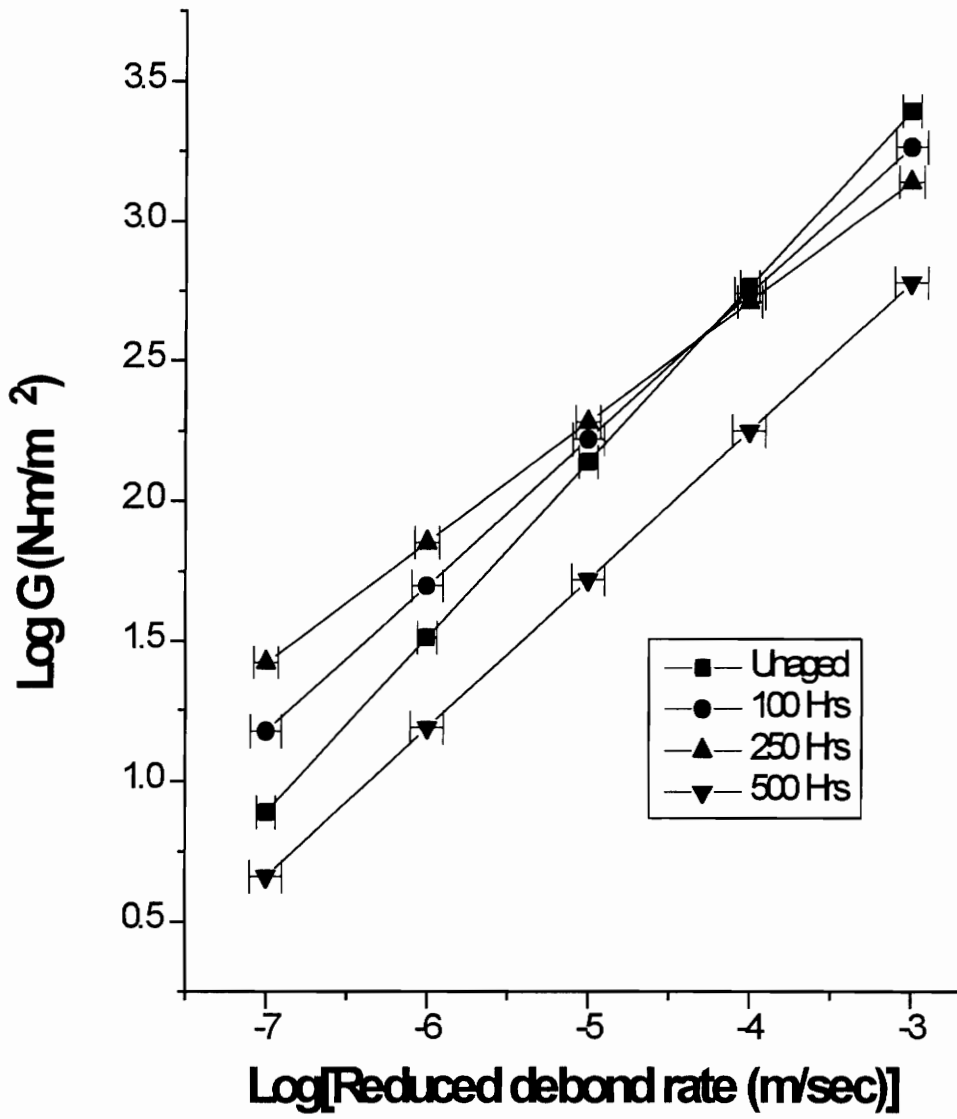


Figure 6.17. Peel master curves for photoaged PVB-30.

# PVB-40

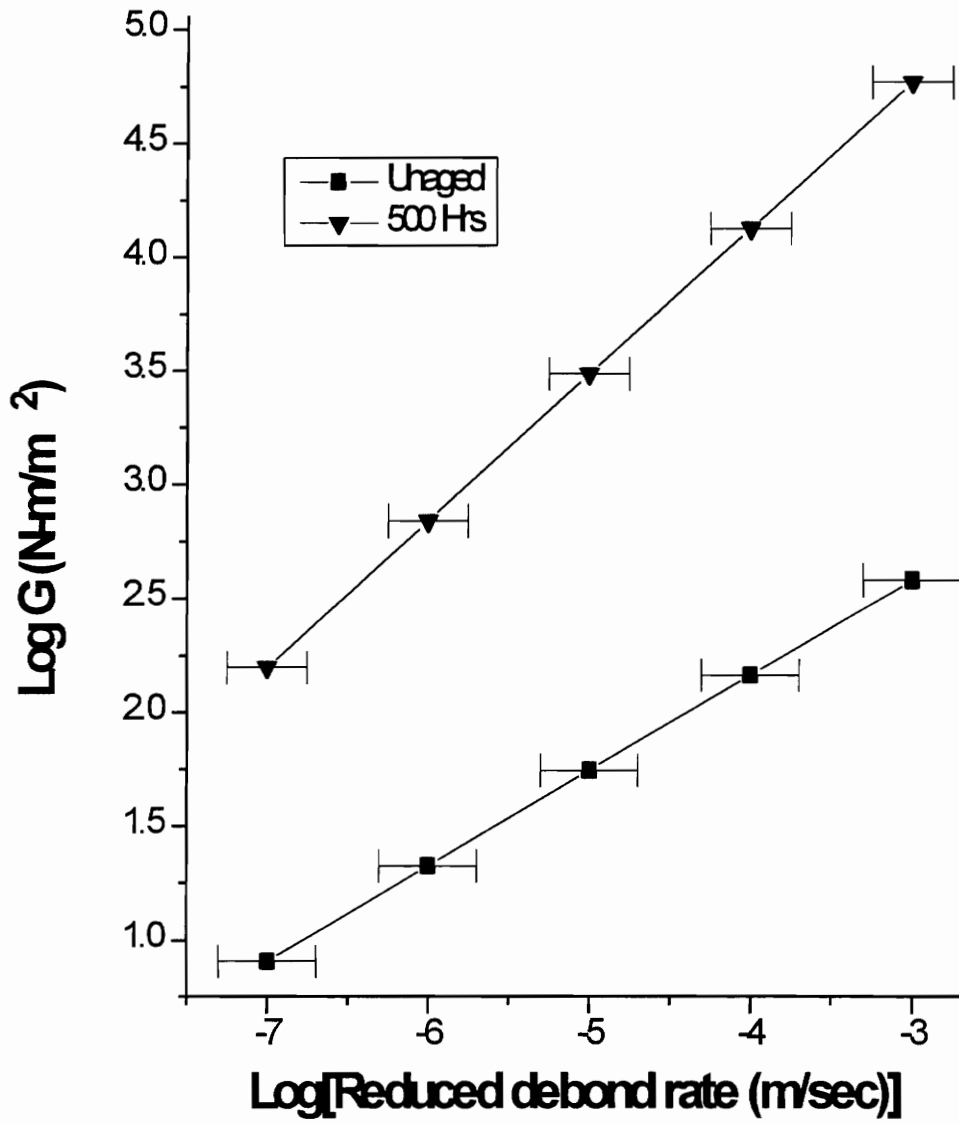


Figure 6.18. Peel master curves for photoaged PVB-40.

## 6.2 Discussion

The experimental results obtained here have demonstrated the tailorability of PVB for a wide range of uses by adjusting the plasticizer content. In its role as an interlayer adhesive, PVB is most suitably plasticized with between 20% and 40% plasticizer. In this range, the polymer behaves as an elastomer at typical testing rates and room temperature. Additionally, the plasticized polymer exhibits a strong adhesion to glass at room temperature and above.

The decrease in peel strength of PVB-10, -20 and -30 with photoageing corresponds to a small decrease in modulus.(section 5.2.1) A decrease in modulus and yield stress would correspond to a decrease in the amount of energy absorbed during mechanical loading such as a peel test. As discussed in the previous chapter, these changes in modulus were not very significant, the testing had a high standard deviation. Only two samples of each formulation and ageing time were peel tested. The lack of a large change in the mechanical properties would suggest that differences described in the peel results were more influenced by sample variation.

The same would hold true for neat PVB and PVB-40. The lack of any change in modulus for neat PVB and PVB-40 would suggest that differences in measured peel strength as a function of photoageing are due to sample variation.

## VII. Conclusions

The mechanical and adhesive properties of neat and plasticized Polyvinylbutyral have been tested. Samples were also subjected to simulated photoageing through exposure to UV radiation and then tested both mechanically and spectroscopically. From these results the following conclusions can be drawn.

- The effect of plasticizer content on the static, dynamic and adhesive properties of polyvinylbutyral has been systematically determined. These results can be used to model the performance of laminated glass structures using PVB as an adhesive interlayer.
- The addition of plasticizer lowers the glass transition temperature of PVB decreasing the modulus dramatically and changing the mechanical behavior from glassy to elastomeric at room temperature.
- Plasticizer content will affect the measured adhesive bond strength between PVB/glass primarily by lowering the glass transition temperature and changing the energy absorption characteristics of the adhesive material at a given test temperature. The primary mode of failure of glass/PVB constructions when tested in peel is cohesive near the interface and thus dependent on the bulk properties of the polymer.

- UV radiation exposure causes the opening of the ring structure within the main backbone and the formation of additional carbonyl bonds in both neat and plasticized PVB which can be tracked using FTIR spectroscopy.
- The level of UV exposure employed in this work was insufficient to cause the dramatic changes in mechanical properties of PVB expected from the results of the chemical characterization work. This is primarily due to the increased thickness of the samples.

## VIII. Future Work

The techniques used in the present study are suitable for determining the long term effects of photoageing on PVB. In order to extend this work and determine actual in-use degradation of safety glass interlayer materials, two additional steps must be taken. First, a UV lamp source with a radiation dosage that is several times stronger than full sunshine should be used to perform the photoageing experiments. The wavelength and energy output of the lamp should be determined at regular intervals during testing. In this way, a correlation between lab experiments and in-use conditions could be determined.

Secondly, samples of the polymer should be exposed in normal sunshine and periodically tested. This should be done on both glass covered and uncovered samples to determine the protection afforded by the glass plate in the layered construction.

Comparing the results from these two separate experiments would provide an estimate of how accurate the lab experiments simulated accelerated ageing and therefore how well this technique predicts long term degrading effects of photoageing on the interlayer adhesives in laminated safety glass.

The study of the adhesive properties of PVB/glass constructions should be extended to include subambient test conditions. Other techniques of measuring bond strength should also be explored including double cantilever beam constructions and impact testing of laminates.

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## VITA

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