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Y-2015

— GLASS TRANSITION TEMPERATURES OF
EPOXY RESINS BY PULSED NUCLEAR
MAGNETIC RESONANCE
SPECTROSCOPY

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MASTER

April 1976

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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

prepared for the **U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION**
under **U.S. GOVERNMENT Contract W-7405 eng 26**

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$2.25

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Date of Issue: **April 21, 1976**
Distribution Category: **UC-25**

Report Number: **Y-2015**

**GLASS TRANSITION TEMPERATURES OF EPOXY RESINS
BY PULSED NUCLEAR MAGNETIC
RESONANCE SPECTROSCOPY**

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Prepared for the US Energy Research
and Development Administration
Under US Government Contract W-7405-eng-26

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ABSTRACT

Pulsed nuclear magnetic resonance spectroscopy has been used to measure the glass transition temperatures of cured epoxy resins. These measurements make it possible to monitor the cure and determine the glass transition temperature as a function of the curing conditions and the concentration of the components. Knowledge of the glass transition temperature of the cured epoxies allows screening of them for a number of uses, including adhesives and coatings operations.

CONTENTS

SUMMARY	4
INTRODUCTION	5
Nuclear Magnetic Resonance Spectroscopy	5
Theory	5
Description of Equipment	7
Chemistry of the Materials	7
Epoxy Resins	7
Curing Agents	9
Versamid Curing Agents	10
Additives	13
Glass Transition Temperature and Chemical/Mechanical Property Relationships	13
Temperature-Dependent Properties of the Polymers	13
Glass Transition Temperature of the Epoxy Resins	15
Glass Transition as a Second-Order Phenomenon	16
Estimation of the Mechanical Properties via the Glass Transition Temperature	16
Correlations of Chemical Structure and the Glass Transition Temperature	18
DETERMINING THE GLASS TRANSITION TEMPERATURE	19
Experimental Procedure	19
Preparation of Samples	19
Nuclear Magnetic Resonance Measurements	19
Discussion of Results	20
CONCLUSIONS AND RECOMMENDATIONS	23
REFERENCES	24
APPENDIX	26
Typical Plots Used in Glass-Transition-Temperature Determinations	26

SUMMARY

Pulsed nuclear magnetic resonance (NMR) spectroscopy has been used at the Oak Ridge Y-12 Plant^(a) to measure the glass transition temperature of cured epoxy resins. Experimentally, the spin-spin relaxation time, T_2 was monitored as a function of temperature. The glass transition temperature, T_g , was taken as that temperature which corresponded to a discontinuous change in the T_2 -versus-temperature plot. Formulations were based on the diglycidyl ether of bisphenol-A resins, fatty polyamide curing agents, and various low-molecular-weight additives. These measurements make it possible to monitor the cure and determine T_g as a function of the concentration of the components of the formulations. Knowledge of the T_g of the cured epoxies allows screening of them for a number of uses, including adhesives and coatings operations.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.

INTRODUCTION

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Theory

Nuclear magnetic resonance (NMR) spectroscopy is a form of radiofrequency (rf) spectroscopy which is based on the magnetic field generated by the spinning of electrically charged nuclei of certain atoms. The sample to be analyzed is placed in a strong magnetic field and exposed simultaneously to an appropriate rf field. The rf induces transitions between slightly different energy states of the nuclei, yielding the spectral information. The frequency, ν , is related to the strength of the external magnetic field, H_0 , the magnetic moment, μ , and the spin number, I , of the nucleus being observed by the expression:

$$\nu = \gamma \frac{H_0}{2\pi} \quad (1)$$

The magnetogyric ratio constant for a particular isotopic species, γ , can be determined by the expression:

$$\gamma = \frac{2\pi\mu}{hI} \quad (2)$$

where h is Planck's constant.

From Equations 1 and 2, it is seen that the energy separation between spin states, $h\nu$, is directly proportional to the applied magnetic field, thus:

$$h\nu = \frac{\mu H_0}{I} \quad (3)$$

The essential parts of an NMR spectrometer are a magnet which produces a high and very homogeneous field and an rf transmitter and receiver.

Two experimental methods are used to observe NMR. One method is called the continuous wave (cw) method in which a very weak rf field is applied continuously to the sample. The energy absorbed is measured as a function of frequency, resulting in a spectrum in the frequency domain. In the second method, the rf field is applied in short, intense pulses. The pulsed technique was used in the transition temperature studies described here, so this method will be discussed in more detail.

The rf pulse rotates all resonant spins through the same angle, as given in the equation:

$$\alpha = \gamma H_1 t_p \quad (4)$$

Where:

- α represents the angle of rotation (radians),
- γ the gyromagnetic ratios ($\text{radians sec}^{-1} \text{ gauss}^{-1}$),
- H_1 the magnetic vector of the rf field (gauss), and
- t_p the duration of the rf pulse (seconds).

After the pulse is turned off, the amplitude of the transient signal is measured as a function of time. The function in the time domain is referred to as a "free-induction decay" (fid); which, with appropriate mathematical manipulation,⁽¹⁾ can yield the same information that is obtainable from a cw spectrum. In addition, the fid gives new information on nuclear-spin relaxation times.

The various types of radiationless transitions, by means of which a nucleus in an upper spin state returns to a lower state, are called "relaxation processes". They control the lifetime in a given spin state and, therefore, the natural linewidth of a spectral line. There are two categories of NMR relaxation processes—spin-lattice and spin-spin relaxation.

Spin-spin relaxation involves a transfer of energy to a neighboring nucleus of the same isotopic species. This process does not equalize the spin population caused by rf absorption. In spin-lattice relaxation, the energy of the nuclear spin system is converted into thermal energy of the molecular system and is, therefore, responsible for maintaining the unequal distribution of spin states.

The efficiency of spin relaxation, which is an exponential process, is expressed in terms of a characteristic time, T , which is the time for a perturbed system of nuclei to attain $1 - 1/e$ ($e = 2.718$) of their equilibrium condition. A large T indicates an inefficient relaxation process. The time associated with the spin-lattice process is designated by NMR spectroscopists as T_1 and that of the spin-spin process as T_2 .

Relaxation times are related to dynamic processes occurring within the sample; thus, the physical state of a substance has a pronounced effect on its relaxation time. An advantage can be taken of this effect and some insight can be gained into changes of the physical state with temperature from relaxation-time measurements.

Solids are relatively rigid aggregations of nuclei in which random movement of the lattice components are negligible, contributing to long T_1 values; but the local fields are large, leading to very small T_2 values. If the linewidth is considered, solids have broad NMR lines; that is:

$$\text{Linewidth (at half height)} = 1/\pi T_2 \quad (5)$$

In liquids, the local fields average out to a small value, and the lines are generally narrow, with factors other than T_2 contributing to the linewidth. The random motions in liquids generally make T_1 in liquids much shorter than in solids.

What type of behavior can be expected if T_2 of a polymer is measured as a function of temperature? It would be found that the behavior depends on the degree of crystallinity of

the polymer. If the material is highly crystalline, there will be almost no increase in T_2 with temperature until the melting point is reached, at which temperature a very large increase in T_2 is observed. An amorphous or partially crystalline material will exhibit a slight increase in T_2 with temperature until the transition region is reached and the increase in T_2 with temperature becomes much more rapid. If the behavior of T_1 is followed with temperature, a minimum would be observed in the transition region. These effects are shown graphically in Figure 1.

Many of the epoxy systems that were studied were not fully cured. In order to prevent altering the systems under study by excessive heat, it was necessary to obtain data as rapidly as practical. This restriction precluded taking T_1 measurements which are much more time consuming to obtain and require going to higher temperatures. The T_1 minimum occurs at temperatures above the "break" in the T_2 curve. Since the T_2 values of the epoxy systems that were studied never exceeded one millisecond, even at 450 K (which was the highest temperature to be attained), data could be collected rapidly from the free-induction decay (fid) following a single 90-degree pulse. (A 90-degree pulse was used because the amplitude of the fid is a maximum and is least affected by small changes in the rf output of the transmitter.)

Description of Equipment

Figure 2 is an overall view of the Bruker Scientific Model BKR-323s pulsed NMR spectrometer used in these studies. The spectrometer has a frequency range of 4 - 100 MHz and a maximum usable field of approximately 22 kilogauss. There is a choice of 1 - 4 pulses and it is possible to control the length of each pulse, the time between pulses, and the repetition rate of the sequence. The pattern can be observed on an oscilloscope or put through a boxcar integrator and recorded on an x-y recorder. The sample is heated or cooled by a temperature-controlled stream of gas.

CHEMISTRY OF THE MATERIALS

Epoxy Resins

A thorough understanding of the chemistry of epoxy resins is required before full use can be made of their outstanding properties. The most important epoxy resins in the technology are based on the reaction products of epichlorohydrin and bisphenol-A:

Figure 1. RELAXATION TIME AS A FUNCTION OF TEMPERATURE FOR A TYPICAL SOLID ORGANIC POLYMER

Table 1
CHARACTERISTICS OF SOME COMMERCIAL EPOXY RESINS

Typical Range of Values		Commercial Designation					
Epoxy Equivalent Weight ⁽¹⁾	Viscosity, Pa·s	Shell (Epon)	Celanese (Epi-Res)	CIBA/Geigy Araldite	Dow (DER)	Reichold (Epotuf)	UCC (Bakelite)
172 - 176	4 - 6	825	508	6004	332	-	ERL-2710
182 - 189	7 - 10	826	509	6005	330	37-139	ERL-2772
185 - 196	12 - 16	828	510	6010	331	37-140	ERL-2774
196 - 208	16 - 20	830	-	6020	2633.17	-	-
232 - 278	(30 - 45) ⁽²⁾	834	515-B	6040	337	-	-
385 - 510	(60 - 75)	836	-	6060	2633.12	37-300	-
425 - 550	(65 - 75)	1001	520-C	6071, 7071	660, 661PR	37-301	EKR-2002
550 - 700	(75 - 85)	1002	522-C	7072	-	37-302	-
875 - 1025	(95 - 105)	1004	530-C	6084	664	37-304	EKR-2003, EKRA-2053
1650 - 2000	(113 - 123)	-	540-C	7097	567	37-307	EKR-2010
2000 - 2500	(125 - 135)	1007	-	6097	668	-	EKRB-2014
2500 - 4000	(135 - 155)	1009	550	6099	669	37-309	EKRA-2018
4000 - 6000	(155 - 180)	1010	560	-	-	-	-

(1) Grams resin/oxirane oxygen.

(2) Numbers in parenthesis are the melting-point ranges in °C.

Curing Agents

Curing agents (also called "hardeners", "activators", or "catalysts") convert the liquid epoxy resins into hard, thermoset solids. Depending on the particular epoxy resin/curing agent, cure often can be effected at room temperature. Aliphatic polyamines, such as triethylenetetramine (TETA) and tetraethylenepentamine (TEPA), are commonly used room-temperature curing agents:

The polyamines are often represented by their linear structural formulas. However, NMR and gas chromatographic evidence indicate that significant quantities of isomeric polyamines containing a tertiary amine may be present.⁽³⁾ For example, the TETA isomer would be:

or, in general:

The importance of such species would be reflected in the degree and type of crosslinking they would provide and the subsequent effect on formulation properties.

The amine curing reaction is based on the ring opening of the epoxide functionality by amine nitrogen:

then:

The curing mechanisms are quite complex and there is a large body of literature on the subject.⁽²⁾

Other commonly used curing agents include the aromatic amines, phenols, organic acids, anhydrides, Lewis acids (such as the boron fluoride complexes),^(2,4) and the modified polyamines [RNHCH₂CH₂(NHCH₂CH₂)_xNH₂]. The modified polyamines provide more convenient mixing ratios than do the neat polyamines and are good room-temperature curing systems. Modifications have been made by adducting the polyamines with alkyl monoepoxides and diepoxides, ethylene and propylene oxide, acrylonitrile, the aldehydes, and by amide formation with various carboxylic acids. Table 2 lists a number of common curing agents.

The choice and amount of curing agent, curing conditions, and addition of modifiers influence the properties of the final product. For optimum properties, the system functionality and potential losses of functionality are considered. Loss of system functionality may occur by the reaction conditions, influence of coreactants, steric factors, and molecular immobility. Typical physical-property values of cured DGEBA resins are listed in Table 3.

Versamid Curing Agents

The versamid series of amidopolyamines are derived from dimerized linoleic acid and aliphatic polyamines. Dimerized linoleic acid (dimer acid) can be represented as the Diels-Alder addition product of 9,11- and 9,12-octadecadieneoic acids:

Table 2
TYPICAL CURING AGENTS FOR EPOXY RESINS

Name	Formula
Triethylenetetramine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
3-Diethylaminopropylamine	$(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
Piperidine
2-Ethyl-4-methylimidazole
2,6-Diaminopyridine
4,4'-Methylenedianiline
<u>m</u> -Phenylenediamine
<u>m</u> -Aminophenol
Boron trifluoride monoethylamine	$\overset{\delta+}{\text{CH}_3\text{CH}_2\text{NH}_2} \cdot \overset{\delta-}{\text{BF}_3}$
Nadic methyl anhydride

Table 3
TYPICAL PROPERTIES OF CURED EPOXY RESINS

Property	Method	Value
Tensile Strength	ASTM 638-52TD	9,000 psi (62 MPa)
Compressive Strength	ASTM D695-54	15,000 psi (103 MPa) Yield 30,000 psi (206 MPa) Ultimate
Flexural Strength	ASTM D 790-49T	18,000 psi (124 MPa)
Modulus of Elasticity	Stress/Strain	400,000 to 600,000 psi (2800 to 4100 MPa)
Poisson's Ratio	-	0.34
Impact Resistance	Izod (ASTM D 256-54T)	0.2 ft lb/in width (69 J/m)

Commercially, the dimer acids are made by the polymerization of acids from various natural oils and have a wide range of viscosities due to various concentrations of linoleic acid, dimer acid, trimer acid, and other polymeric species.

Reactions of dimer acid with polyamines, such as TETA and TEPA,⁽⁵⁾ yield the amidopolyamine products commonly called polyamide resins:

These materials are manufactured under the trade name Versamid (General Mills). Table 4 lists some typical properties of the Versamids commonly used as epoxy-resin curing agents. The amine value and viscosity are influenced chiefly by their free polyamine content.⁽³⁾

With DGEBA resins, the Versamids yield cured products of greater flexibility than do the unmodified polyamines. Moreover, the Versamids can be used in a variety of proportions with DGEBA in order to obtain different properties. The extent to which the DGEBA/Versamid ratios can be varied without loss of desirable properties is limited by chemical as well as physical considerations. Calculations have indicated that DGEBA/44 wt % Versamid 125, and DGEBA/20 wt % Versamid 140 are approximately stoichiometric compositions. The relative amounts of Versamid can be increased to obtain more flexible materials. This fact is borne out in the data of Table 5 which presents the range of hardnesses obtained by varying the Versamid 125 content in DGEBA/Versamid 125 formulations.

Table 4
PROPERTIES OF VERSAMIDS
USED AS EPOXY RESIN
CURING AGENTS

Designation	Viscosity (Pa-s)	Amine Value ⁽¹⁾
Versamid 115	80.0 - 120.0 ⁽²⁾	210 - 230
Versamid 125	40.0 - 60.0 ⁽³⁾	270 - 320
Versamid 140	9.0 - 15.0 ⁽³⁾	360 - 390

(1) Number of milligrams of KOH equivalent to the amine content of one gram of material.

(2) At 40° C.

(3) At 25° C.

Table 5
HARDNESS OF CURED DIGLYCIDYL ETHER
OF BISPHENOL-A AS A FUNCTION
OF THE VERSAMID 125 CONTENT

Versamid 125 (phr) ⁽¹⁾	Hardness ⁽²⁾	
	Barcol	Shore A
66	60 - 65	-
100	20 - 25	-
150	-	90
180	-	85
234	-	50
300	-	30
400	-	5

(1) Parts per hundred parts by weight of epoxy resin.

(2) From General Mills technical literature.

The Versamid curing agents are used chiefly with DGEBA resins as general-purpose adhesives and coating formulations. The curing agents are used at greater than stoichiometric amounts to provide increased impact resistance. Chemical and solvent resistance of DGEBA/Versamids are lower than obtained with the aliphatic-polyamine-cured systems;⁽⁶⁾ however, they show improvement in water resistance. The Versamid/epoxy formulations in this report are currently under evaluation as protective coating systems. Reports of this evaluation will be issued later.

Additives

Additives were included in the Epon 828/Versamid 140 formulations because of the potential surface-active properties they would impart to the coating system. Those under investigation were mainly difunctional aliphatic compounds and silane coupling agents. This report is concerned only with those additives listed in Table 6.

GLASS TRANSITION TEMPERATURE AND CHEMICAL/MECHANICAL PROPERTY RELATIONSHIPS

Temperature-Dependent Properties of the Polymers

It is fundamental in the study and synthesis of polymers to develop meaningful relationships between polymer chemistry and mechanical properties. Knowledge of the mechanical properties of polymers is essential in any application where they are integral parts of structural materials. The end uses of most plastics, rubbers, and fibers are governed chiefly by their mechanical properties. It is essential for the polymer chemist to know how mechanical behavior is related to the chemical structure. With such knowledge, materials could be tailor made with any desired characteristics.

Properties of the amorphous polymers are highly dependent upon the molecular motion of their chains. The amount of motion and, hence, properties will vary as a function of temperature. For a given polymer, very little motion may occur at very low temperatures and its properties are characterized by stiffness, hardness, or brittleness. At slightly higher temperatures, the increased motion of chains will yield a corresponding decrease in these

Table 6
ADDITIVES USED IN THIS STUDY

Name	Formula
Ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
1,4-Diaminobutane	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
1,2-Diaminocyclohexane
1,7-Diaminoheptane	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
γ -Aminopropyltriethoxysilane (A-1100 Silane) ⁽¹⁾	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$
Methyltrimethoxysilane (Z-6070 Silane) ⁽²⁾	$\text{CH}_3\text{Si}(\text{OCH}_3)_3$
β (3,4-Epoxy-cyclohexyl)- ethyltrimethoxysilane (A-186 Silane) ⁽¹⁾
γ -Glycidyloxypropyltrimethoxy- silane (A-107 Silane) ⁽¹⁾
N-(β -aminoethyl)- γ -aminopropyl- trimethoxysilane (Z-6020 Silane) ⁽²⁾	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$

(1) Product of the Union Carbide Corporation.

(2) Product of the Dow-Corning Corporation.

properties. At an even higher temperature, the polymer may become limp, flexible, or otherwise show the phenomena of viscoelasticity characteristic of many polymers. The temperature which indicates the region of discontinuous change between brittleness and viscoelasticity is called the "glass transition temperature" (T_g).

T_g is probably the one most useful bit of information that can be obtained on a polymer. T_g is important not only in that the type of polymer behavior is indicated at that temperature; but (more importantly) from T_g , considerable information about the mechanical behavior of the polymer at a variety of temperatures can be derived. Relationships have been developed between T_g and the chemical structure, modulus, permeability, and adhesive strength of a polymer, thus giving the polymer chemist powerful tools in the development of chemical/mechanical property relationships.

At temperatures lower than the T_g , other transitions may occur that are produced by the motion of short sections of the main chain or of side chains. Although some characteristics of the glassy state (such as brittleness) occasionally may occur only below one of the lower

transitions,⁽⁷⁾ it has been proposed⁽⁸⁾ that the transition of the highest temperature be called " T_g ". Transitions are often denoted by⁽⁹⁾ T_α , T_β , T_γ , ... in order of descending temperature, but there is a lack of uniformity in the designations in the literature.

Glass transition temperatures are often obtained from measurements of such properties as volume, heat capacity, hardness, deflection, elastic modulus, or refractive index as a function of temperature. These and other properties show changes in slope at the glass transition when they are plotted as a function of temperature. Relaxation times measured by NMR are more directly related to molecular motion than most of these other physical properties.

Glass Transition Temperature of the Epoxy Resins

Generally, cured epoxy resins at ambient temperature are in a glassy state where large-scale molecular motion does not occur. Instead, small groups of atoms move against the local restraints of secondary bond forces, such as the rotation of the isopropylidene methyl groups. The glass transition corresponds to the onset of motion of larger segments of the molecule and manifests itself as a change from a glassy state to a rubbery state. Literature values of T_g for a number of epoxy resin systems are listed in Table 7.

Table 7
GLASS-TRANSITION-TEMPERATURE VALUES
OF CURED EPOXY RESINS

Curing Agent	Amount ⁽¹⁾ (phr)	Curing Conditions (hrs/ $^{\circ}$ C)	T_g (K)
Triethylenetetramine	13	168/25	388
Diethylaminopropylamine	7	24/100	373
Piperidine	6	15/23 + 5/46 + 15/74	348
Methylenedianiline	26	1.5/100	410
m-Phenylenediamine	14.5	2/85 + 16/150	428
2,6-Diaminopyridine	14.3	2/120 + 2/204	383
m-Aminophenol	18.2	2/120 + 2/204	401
2-Ethyl-4-methylimidazole	10	8/55	383
Boron trifluoride monoethylamine	3	16/93 + 170/150	483
Nadic methyl anhydride	84	4/80 + 15/150	426

(1) Parts per hundred parts DGEBA, by weight.

Experimentally, T_g depends on the time scale of the experiment in which it is measured. Because molecular segmental motion occurs at definite rates, test methods which subject the polymer to a rate of loading faster than the polymer is capable of adapting to will give higher values of T_g than methods which load the polymer slowly (that is, at a rate less than its relaxation time). The commonly used slow test methods for epoxy resins are the deflection temperature (DT) and the thermal expansion rate.

Studies of the molecular motion of epoxy resins by Larsen and Strange⁽¹⁰⁻¹²⁾ suggest the feasibility of T_g determinations by pulsed NMR. This report describes such a method for determining this transition temperature in certain epoxy resin systems.

Glass Transition as a Second-Order Phenomenon

The glass/rubber transition shows some resemblance to a second-order transition. In thermodynamics, second-order transitions involve a discontinuous change in a secondary thermodynamic quantity such as the expansion coefficient or heat capacity, and T_g is often determined by such measurements. However, it has not been proved conclusively that T_g is a thermodynamic parameter.

Gibbs and DiMarzio⁽¹³⁾ developed a statistical model which predicted the glass transition and some of its characteristics. However, verification of the thermodynamic interrelation among changes in heat capacity, expansion coefficient, and compressibility at the T_g has been successful only occasionally.^(14,15)

If T_g were a real second-order transition, the following relationship would hold:

$$\Delta C_p \Delta k = T_g V_g (\Delta \alpha)^2, \quad (11)$$

where:

T_g represents the glass transition temperature,

C_p the heat capacity at constant pressure,

V_g the molar volume at the T_g ,

$\Delta \alpha = \alpha_l - \alpha_g$ the difference in the thermal expansion coefficient at the T_g ,

$\Delta C_p = C_p^l(T_g) - C_p^s(T_g)$ the difference in the molar heat capacity at the T_g , and

$\Delta k = k_l - k_g$ the difference in the compressibility at the T_g .

In fact, the data of Breuer and Rehage⁽¹⁵⁾ confirm the relationship. Unfortunately, there is not a large amount of accurate data to thoroughly test the validity of the equation. Most available data show large deviations, so that the calculations lead merely to the correct order of magnitude.⁽¹⁶⁻¹⁸⁾ Staverman⁽¹⁹⁾ and Breuer and Rehage⁽¹⁵⁾ concluded that T_g is not a real second-order transition, mainly because they felt the glassy state is not completely defined by the normal state variables, namely: pressure, volume, and temperature.

Estimation of the Mechanical Properties via the Glass Transition Temperature

T_g can be used to make estimations of the mechanical-property parameters and the time/temperature dependence of polymers. A reasonably good estimation of the shear modulus (rigidity), G , of a polymer at room temperature (298 K) is the application of the empirical relationship:⁽²⁰⁾

$$G^{298} = G_g^{298} + x_c^2 [G_c^{298} - G_g^{298}], \quad (12)$$

where:

X_C represents the degree of crystallinity,

G_C the shear modulus of the fully crystalline polymer, and

G_g the shear modulus of a fully glassy polymer. In Equation 12:

$$G_C^{298} \cong \frac{T_m - 298}{100} \cdot 10^9, \text{ and} \quad (13)$$

$$G_g^{298} \cong \frac{3}{1 + \frac{600}{T_g}} \cdot 10^9. \quad (14)$$

G_g^{298} is neglected if $T_g < 298$ K. T_m is the melting temperature, in degrees kelvin, of the crystalline polymer; G_C^{298} and G_g^{298} are in pascals. Young's modulus (E) and the bulk modulus (K) can likewise be estimated in light of the relationships:

$$E - 3K(1 - 2\nu) = 2G(1 + \nu), \quad (15)$$

where ν represents Poisson's ratio. If Poisson's ratio is not known, the rule of thumb (~ 0.33 for glassy polymers, ~ 0.40 for semi-crystalline polymers, and ~ 0.49 for elastomers) often gives satisfactory results.

Effects of T_g on the mechanical properties have been further demonstrated by the observation of a direct relationship between T_g of an epoxy adhesive and its lap-shear strength to metal at elevated temperatures.⁽²¹⁾ The indication is that T_g measurements are effective screening methods for adhesive formulations.

Above the T_g , the stress relaxation and creep behavior of amorphous polymers obey the time-temperature superposition principle. That is, time and temperature are equivalent to the extent that data at one temperature can be superimposed upon data taken at a different temperature, merely by shifting curves. The superposition is made by use of the so-called shift factor, α_T . The generalized formula for the shift factor is, according to Williams, Landel, and Ferry:⁽²²⁾

$$\log \alpha_T = \log t/t(T_g) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)}. \quad (16)$$

In this equation, T_g is used as the reference temperature.

T_g also has been shown to be essential to permeability calculations. Permeation of gases is of great practical importance in the manufacture and processing of polymers and especially in their subsequent use as protective coatings. The permeability (P) of a polymer to a gas is the product of two factors: the solubility (S) and the diffusivity (D) in and through the polymer; ie:

$$P = S \cdot D. \quad (17)$$

Permeability can be directly measured as the rate of transfer of a gas through a polymer film and is expressed per unit area, thickness, and pressure difference across the film. However, S and D can be reasonably estimated if the critical temperature and diameter of the permeating molecules and the structure, X_c and T_g , of the polymer are known. A good treatment of the calculations is given by Van Krevelen. (20)

Correlations of Chemical Structure and the Glass Transition Temperature

Several authors have proposed correlations between the chemical structure of T_g of polymers. Their methods are usually based on the assumption that functional groups in the repeating units provide weighed additive contributions to the T_g . The general form for the correlation is:

$$T_g = \frac{\sum_i S_i T_{gi}}{\sum_i S_i} \quad (18)$$

where:

T_{gi} represents the specific contribution to T_g in degrees kelvin of a given functional group and,

S_i represents a weight factor attributed to a given functional group. Several authors (23 - 26) have examined methods for applying the equation or modifications of it to a variety of polymers, mostly linear polymers with and without side chains. As indicated in Table 8, the correlations can be very good. Unfortunately, with cross-linked polymers such as cured epoxy resins the correlations are not as good.

Table 8
EXPERIMENTAL AND CALCULATED VALUES OF THE GLASS TRANSITION TEMPERATURE FOR A NUMBER OF POLYMERS
[After D. W. Van Krevelen, *Properties of Polymers - Correlations with Chemical Structure*; Elsevier Publishing Co, Amsterdam (1972)]

Polymer	T_g	
	Experimental	Calculated
Polypropylene	253	253
Polystyrene	373	373
Polyisobutene	198	198
Polyvinyl fluoride	253/313	250
Polyvinyl chloride	356	354
Polyvinylidene fluoride	233/286	235
Polyvinylidene chloride	255/288	250
Poly 1,2-difluoro ethylene	323/371	330
Polychlorotrifluoroethylene	318/325	325
Poly- α -methyl styrene	390/465	450
Polybutadiene, cis	171	170
Polybutadiene, trans	259	260
Polymethylene oxide	190/243	225
Polyethylene oxide	206	207
Polytetramethylene oxide	185/194	192
Polyethylene adipate	203/223	230
Polyethylene terephthalate	343/350	347
Poly 4,4'-isopropylidene diphenylene carbonate	414/423	392
Polyhexamethylene adipamide	318/330	335
Polydecamethylene sebacamide	333	312
Polytetramethylene hexamethylene diurethane	303	319
Polyhexamethylene dodecamethylene diurea	322	323
Polydimethyl siloxane	150	150
Polymethyl acrylate	279/282	280
Polyethyl acrylate	249/252	250
Polyheptyl acrylate	213	213
Polyhexadecyl acrylate	308	311
Polyisopropyl acrylate	262/284	284
Polymethyl methacrylate	378/399	378
Polyethyl methacrylate	285/338	315
Polyhexyl methacrylate	256/268	244
Polyhexadecyl methacrylate	288	274

DETERMINING THE GLASS TRANSITION TEMPERATURE

EXPERIMENTAL PROCEDURE

Preparation of Samples

Samples for T_g measurements were cylindrical rods, nominally 0.635 cm (0.25 in) in diameter, cast from various Epon 828/Versamid/additive formulations and cut to 0.9 to 1.1 cm in length. The Epon 828 and Versamid 140 were vacuum degassed separately at 80° C and then allowed to cool to room temperature prior to use. The additives were used as supplied by the vendors.

In a typical experiment, a 2.00-gram portion of additive was mixed well into 49.00 grams of freshly degassed Versamid 140 at room temperature. To this mixture was added 49.00 grams of Epon 828 and the formulation again mixed for approximately two minutes. Air bubbles from the mixing operation were removed by centrifugation. The clear mix was poured into cylindrical molds made from 10 - 15-cm (4 - 6-in) lengths of 0.635-cm (0.25-in)-inside-diameter polystyrene tubing which was previously mold released with a polysiloxane wax. The tubing was sealed at the ends during the curing cycle. Cure was accomplished at room temperature, at 70° C (in a laboratory oven), or after a cycle combining the two temperatures. At various times, rods were cut to length (0.9 to 1.1 cm), removed from the polystyrene mold, sealed in vials, and cooled in a freezer at -20° C to stop the curing reaction.

Nuclear Magnetic Resonance Measurements

The sample to be analyzed was removed from the freezer and its length measured. After a five-minute warmup at room temperature it was placed in a special, thin-walled, flat-bottom tube and positioned in the center of the transmitter/receiver coil. A brisk stream of air at 300 K was passed over the sample. The timer was started and the temperature was increased by 10 K every 150 seconds until the final temperature of 450 K was reached. During the initial 135 - 140 seconds of each interval while the sample was attaining thermal equilibrium, minor spectrometer and scope adjustments were made. During the final 10 - 15 seconds at a particular temperature, several fids were observed on the high-frequency oscilloscope, and the time was measured for the fid to decrease in amplitude half way from its initial to its equilibrium value. The half-time measurement ($T_{1/2}$) was chosen rather than estimating T_2 since this parameter could be read from the scope screen more rapidly and accurately.

T_2 is related to $T_{1/2}$ as follows:

$$M_t = M_0 e^{-t/T_2}, \quad (19)$$

where:

M_0 represents the magnetization (amplitude of fid immediately following a 90-degree pulse), and

M_t the magnetization at time t after the 90-degree pulse.

$$\text{For } t = T_2, M_t = M_0 e^{-1} = M_0/e. \quad (20)$$

T_2 is thus the time required for the magnetization to decay to $1/e$ ($1/2.718$ or 36.8%) of its initial value. The $T_{1/2}$ measured in this study was the time for the magnetization to decay to $1/2$ its initial value, or $M_t/M_0 = 0.5$. Using Equation 19:

$$0.5 = e^{-T_{1/2}/T_2}, \text{ or} \quad (21)$$

$$\ln 0.5 = -T_{1/2}/T_2, \text{ or} \quad (22)$$

$$-0.69315 = -T_{1/2}/T_2, \text{ or} \quad (23)$$

$$T_2 = T_{1/2}/0.69315 = 1.443 T_{1/2}. \quad (24)$$

Since the major interest in this study was in the transition temperature, $T_{1/2}$ values were plotted as a function of temperature. Some representative graphs are presented in the Appendix. The plotter accessory of a Hewlett Packard 9220A programmable calculator was used to plot the points. All that was required was entering the $T_{1/2}$ values in sequence and setting the coordinates on the plotter.

DISCUSSION OF RESULTS

In this study there were two different ratios of Epon 828 resin to the Versamid 140 curing agent: 50/50 and 70/30. The experimental data are presented in Tables 9 through 11.

The 50/50 mixtures were all sufficiently cured to obtain the T_g values, although the specimens cured at room temperature evolved some amine during the measurements. The 70/30 mixtures were not all sufficiently cured to obtain the T_g values. Only data on the 70/30 samples that had been heated at 70°C for at least three hours are included in Table 11. Samples which had been kept at room temperature for up to six days and a sample which was held at 70°C for only one hour, cured as they were heated during the NMR observations, and no valid transition data could be obtained.

The Epon 828/Versamid 140 (50/50) mixtures had lower T_g values than the comparably cured 70/30 mixtures. The 50/50 mixtures achieved their equilibrium T_g values in 1 - 2 hours at 70°C and 5 - 6 days at room temperature. Longer cure periods did not produce significant differences. A 50/50 mixture cured at 70°C for a few hours had a higher T_g than the same composition cured for over a month at ambient temperature.

Table 9
EPON 828/VERSAMID 140 (50/50) TWO
WEIGHT PERCENT ADDITIVE CURED
AT ROOM TEMPERATURE

Cure Time (days)	T_g (K)
<u>Ethylenediamine</u>	
6	335
18	335
33	331
47	330
<u>1,4-Diaminobutane</u>	
6	339
18	339
33	338
47	337
<u>1,2-Diaminocyclohexane</u>	
1.67	336
8	340
22	343
36	343
<u>1,7-Diaminoheptane</u>	
5	340
17	341
32	342
46	342

Table 10
EPON 828/VERSAMID 140 (50/50) TWO
WEIGHT PERCENT ADDITIVE CURED
AT 70° C

Cure Time (hrs)	T _g (K)
<u>Ethylenediamine</u>	
2	342
68	342
116	343
236	342
<u>1,4-Diaminobutane</u>	
5	360
48	355
166	354
350	358
<u>1,2-Diaminocyclohexane</u>	
1	358
185	355
336	358
528	360
672	357
<u>1,7-Diaminoheptane</u>	
50	360
115	358
300	357
456	358

Table 11
EPON 828/VERSAMID 140 (70/30) WITH VARIOUS ADDITIVES,
CURE TEMPERATURES, AND CURE TIMES

Additive Compound		Time at Room Temperature	Time at 70° C	T _g
(designation)	(wt %)	(hrs)	(hrs)	(K)
None		16	16	368
None		48	24	381
None		0	3	358
None		0	5	365
None		0	16	369
Z-6020	0.1	24	288	386
Z-6020	0.5	24	288	386
Z-6020	1.0	24	288	383
Z-6020	5.0	24	288	376
A-1100	5.0	0	96	376
A-1100	5.0	24	24	366
A-187	5.0	0	96	372
A-187	5.0	24	24	366
A-186	5.0	0	96	374
A-186	5.0	24	24	372
Methyltrimethoxysilane	5.0	0	96	372
Methyltrimethoxysilane	5.0	24	24	367

The data in Tables 9 and 10 indicate that only the addition of ethylene-diamine (which has a high NH_2 content for a given weight) to the 50/50 material produced a significant reduction in the T_g . Some data obtained previously for an Epon 828/Versamid 140 (50/50) mixture cured from 1 - 24 hours at 100°C gave a T_g of 361 K, which is comparable to values obtained for a 70°C cure in the present study.

In the Epon 828/Versamid 140 (70/30) series, the length of time at 70°C influenced the T_g , as seen in Table 11. There were not enough data to ascertain whether room-temperature curing prior to heating to 70°C affected the T_g values. Addition of 5 wt % of a silane adhesion promoter or coupling agent reduced the T_g , but the addition of one percent or less did not alter the T_g significantly. Some older data on an Epon 828/Versamid 140 (67/33) mixture that had been cured for 24 hours at 100°C gave a T_g value of 397 K, which is higher than any results on the 70/30 material that had been cured at 70°C .

CONCLUSIONS AND RECOMMENDATIONS

Pulsed NMR is an important tool for obtaining reliable measurements of the glass transition temperatures of polymers. The measurements provide the means for screening polymers for a number of applications such as their use in adhesives and coatings. It is recommended that pulsed NMR be used for future evaluations of polymers, including the polyurethanes, polysulfides, polyolefins, and acrylics. Use of ^{19}F as the observed nucleus permits this method to be used for T_g measurements on fluorocarbons.

The signal-to-noise ratio in these studies was adequate, but could be improved by the use of a transient recorder coupled to a signal averager. This arrangement would also permit the use of smaller samples, and thus more readily attain thermal equilibrium. T_g values can currently be measured over a temperature range of 220 - 410 K. The temperature range could be increased with properly designed transmitter/receiver inserts. The experiments described here were performed with off-the-shelf components.

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APPENDIX

TYPICAL PLOTS USED IN GLASS-TRANSITION-TEMPERATURE DETERMINATIONS

Figure A-1. POLYMER TRANSITION TEMPERATURE.
(Sample T26-2)

Figure A-2. POLYMER TRANSITION TEMPERATURE.
(Sample T27-4)

Figure A-3. POLYMER TRANSITION TEMPERATURE.
(Sample T23-2)

Figure A-4. POLYMER TRANSITION TEMPERATURE.
(Sample T18-4)

Figure A-5. POLYMER TRANSITION TEMPERATURE.
(Sample 66A-3)

Figure A-6. POLYMER TRANSITION TEMPERATURE.
(Sample 66D-2)

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