

The Glass Transition Temperature of a Filled Binder by Nuclear Magnetic Resonance and Thermal Mechanical Analysis

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Synopsis

The glass transition temperatures of a binder and filled binder were determined by wide line proton nuclear magnetic resonance and by thermal mechanical analysis. The NMR study indicated only one transition temperature for the binder and three transition temperatures for the filled binder. TMA data gave two transition temperatures each for the binder and for the filled binder. These transition temperatures in the filled binder were interpreted as representing two phases: one for the filler-oriented binder and one for the bulk phase. A comparison of the transition temperatures of the binder and filled binder indicates that the transition temperature of the former is raised by the presence of the filler. It was also found that the presence of water lowered the transition temperature of the filled binder used in this work.

INTRODUCTION

The glass transition temperature is one of the most important parameters for polymer characterization. At this point, many properties of polymers begin to change with temperature at a different rate. For example, dynamic shear modulus, which has a high value below the glass temperature, begins to drop rapidly; elongation at break, on the contrary, which has been slowly rising, begins to sharply increase in value; and the coefficient of thermal expansion shows a discontinuous rise to a new value. Several experimental techniques have been used to measure glass transition temperatures, a traditional one being the change in specific volume as a function of temperature. A more recent and sensitive technique has employed the determination of nuclear magnetic resonance line widths as a function of temperature.¹⁻³

In the last decade, a considerable amount of work has been reported on the effects of the filler on the physical properties of polymeric composites. In the case of filled rubbers, some investigators have reported changes in thermodynamic properties^{4,5} and mechanical properties^{6,7} due to the presence of varying amount of filler. Until recently, there has been little information in the literature concerning the effect of fillers on transition temperatures. It has been observed by some workers that with increasing filler concentration the glass transition temperature increases.⁸⁻¹¹ On the

other hand, some researchers have observed no changes in the glass transition temperature with variations in filler content.^{12,13} Kumins and Roteman¹⁴ observed a decrease in the glass temperature of TiO₂-filled poly(vinyl acetate-vinyl chloride) at certain filler content. These physical changes have been explained qualitatively in terms of a two-phase system.^{10,15-18} One phase, which consists of polymer near the filler interface, has different conformational properties and is restricted in its molecular motion by interaction with filler. The other phase consists of polymer not in the immediate vicinity of the filler interface and has molecular properties similar to those of the pure polymer. Recently, multiple phases in filled polymers have been detected by proton nuclear spin relaxation studies.¹⁶⁻¹⁷ We wish to report some results of the effect of filler and moisture on the glass transition temperature of a filled binder as determined by thermal mechanical analysis (TMA) and wide-line proton nuclear magnetic resonance (NMR).

EXPERIMENTAL RESULTS

The binder with a molecular weight around 5000 was prepared from a polyester containing 50% by volume styrene. The filled binder contained 75% by weight potassium perchlorate (200 μ).

The nuclear magnetic resonance experiments were performed at Howard University. Line shape measurements were performed with a regenerative spectrometer operating at 25.0 MHz. Measurements were obtained from room temperature to -110° C. At each temperature of measurement, it was found that an hour was required for temperature equilibration to be attained in the interior of the binder and filled binder. From the line shape, the line width ΔH , in gauss, was determined and plotted against temperature. The transition temperature was obtained by plotting the slope

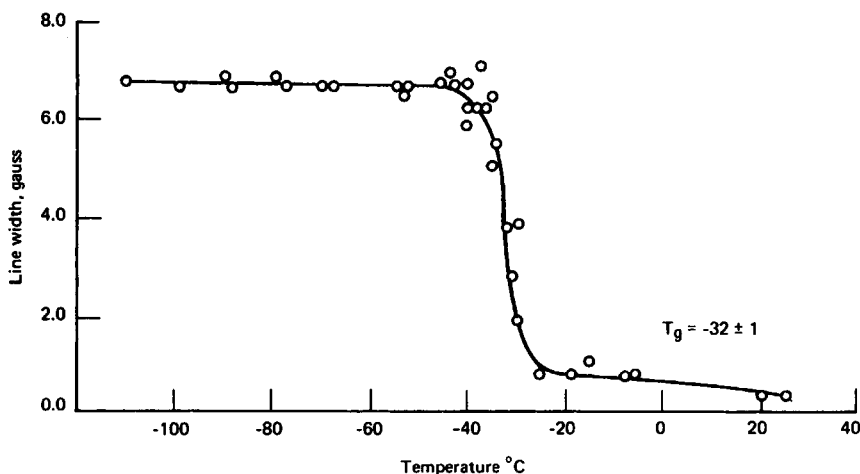


Fig. 1. Line widths vs. temperature for binder.

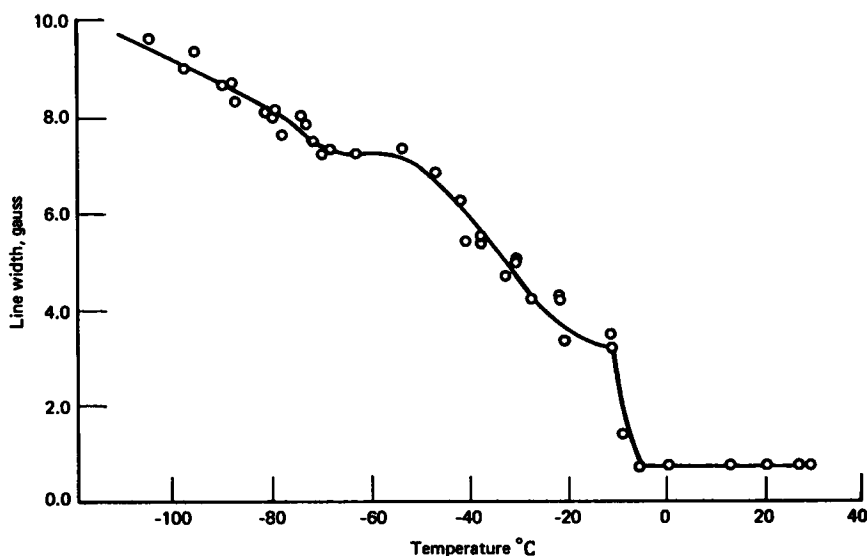


Fig. 2. Line widths vs. temperature for filled binder.

$\Delta H/\Delta t$ versus the temperature to determine the temperature at which the maximum slope occurred. TMA measurements were obtained with a du Pont 941 TMA module connected to a du Pont 900 thermal analyzer. Samples were run from -100° to $+100^{\circ}\text{C}$ at a heating rate of $5^{\circ}\text{C}/\text{min}$ and a ΔT setting of 0.2 to 0.004 mv/in.

In the temperature range of 25° to -105°C , an NMR study indicated only one transition temperature (-32°C , Fig. 1) for the binder and three transition temperatures (-9° , -30° , and -74°C , Fig. 2) for the filled binder. For the binder, TMA data gave two transition temperatures at

TABLE I
Transition Temperatures for Filled Binder and Binder by Nuclear
Magnetic Resonance and Thermal Mechanical Analysis

	Filled binder			Binder
	Original ^a	Wet ^b	Dried	
NMR	{ -43°C -74°C	{ — —	{ -9°C ^d -30°C ^d -74°C ^d	{ -32°C ^e —
TMA	{ -28°C 27°C	{ -54°C 30°C	{ -18°C ^e 25°C ^e	{ -38°C 22°C

^a Sample prepared at Naval Ordnance Station.

^b Sample exposed to water vapor for two days at room temperature.

^c Sample dried for seven days at 80°C in vacuum oven.

^d Sample dried at 108°C for 75 hr and sealed under vacuum.

^e The transition temperature of the uncured binder consisting of polyester and 50% by volume styrene is less than -93°C . For the polyester without styrene, the transition temperature is -49°C .

-38° and 22°C , respectively, whereas for the filled binder transitions at -18° and 25°C were observed. A comparison of transition temperatures of the binder and filled binder obtained by NMR and TMA are listed in Table I.

It is believed that filled binders may have two transition temperatures: one for the filler-oriented binder and one for the bulk of the continuous phase. The transition temperature for the filler-oriented binder is expected to occur at a higher temperature than the unmodified bulk phase because of the increase in rigidity of the polymer in the vicinity of the filler. The temperature -9°C , obtained by NMR, is assigned to the filler-oriented binder. A change in mechanical properties (elongation at break) has also been observed to occur at -7°C . From the TMA data, the temperature -18°C is also assigned to filler-oriented binder, but the value in the range of 25°C is unexplained. The latter is observed in both filled and unfilled binder. Further discussion of the difference between the temperatures (-9° and -18°C) assigned to the filler-oriented binder will be presented later. For the filled binder, NMR shows a transition at -30°C which coincides with the transition at -32°C for the binder. TMA measurements did not indicate a transition in this temperature range for the filled binder. Since there are more than one type of bond and groups in the polymer chain, a number of second-order temperatures may be observed. The weak transition at -74°C may be one. This weak transition may be present in the binder at a much lower temperature (less than -100°C).

Galperin and Arnheim¹⁹ have suggested that water alters the packing of polymer chains in unfilled poly(vinyl acetate) and thereby changes intermolecular forces, with resultant changes in tensile properties of the polymer. These investigators have also reported that in TiO_2 -filled poly(vinyl acetate) the interaction of filler with polymer is also affected by water. Kumins, Roteman, and Rolle²⁰ reported that crystalline solids such as TiO_2 incorporated with a film of poly(vinyl acetate-vinyl chloride) absorbed relatively large amounts of water vapor on the surface. To our knowledge, the effect of moisture on transition temperatures of filled polymers has not been reported. If the transition temperatures (Table I) for a wet and dried sample of the filled binder are compared, it seems that the wet sample shows a decrease in transition temperature from -18° to -54°C by TMA and from -9° to -43°C by NMR. When the sample of filled binder was allowed to stand over water for two days, NMR measurements were difficult to obtain because the water line interfered with the NMR absorption of the polymer. Nevertheless, it does seem that moisture lowers the transition temperature of the filled binder. The difference between the transition temperatures (-9° and -18°C) of the dried, filled binder determined by the two different methods lies in the fact that the sample was exposed to the atmosphere before the TMA measurements were made. Therefore, the sample may have picked up some moisture. The sample used for NMR measurements was dried and sealed under vacuum.

Brittleness tests were run on samples which had been stored over water at ambient temperatures. The weight increase was approximately 0.2%. These moist samples were markedly different from dried samples. Elongation at break increased from about 10% for dried samples to 40% for moist samples. Galperin and Arnheim¹⁹ have observed a similar behavior for filled poly(vinyl acetate) stocks. In our experiments, it was noted that the change in behavior caused by water addition was reversible. The effect of moisture was confined to the filled binder only and was not observed with the binder. It is postulated that the effect of moisture is caused by its effect on the adhesion of the binder to the filler surface.

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