Effects of Moisture and Stoichiometry on the Dynamic Mechanical Properties of a High-Performance Structural Epoxy

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Synopsis

Dynamic mechanical measurements have been made on a 4,4'-diaminodiphenyl sulfone-cured tetraglycidyl 4,4'-diaminodiphenylmethane epoxy (TGDDM-DDS). There are basically three transitions on the mechanical spectra that have been identified, and the effects of moisture uptake and amount of DDS on these transitions were examined. The dynamic mechanical behavior of the same epoxy with 60% carbon fiber loading was also studied, providing further elucidation on the nature of the transitions observed with this system.

INTRODUCTION

The recent use of epoxy polymers in composite parts for load-bearing structural applications makes the evaluation of their viscoelastic properties an important consideration since the properties of these materials depend both on the temperature and the duration (or frequency) of the applied load or deformation. This viscoelastic behavior, which is typical of polymers, has prompted the use of oscillating mechanical fields to characterize their mechanical response as a function of temperature.

In the present study the dynamic mechanical properties of a commercial epoxy system based on tetraglycidyl 4,4'-diaminodiphenylmethane epoxy (TGDDM) cured with 4,4'-diaminodiphenyl sulfone (DDS) without additional catalyst was investigated. This resin system was chosen because of its commercial importance to the aerospace industry and because in the past it has been the focus of detailed investigations.[1,2,11,12]

Previous static experiments have shown that this epoxy system is sensitive to absorbed moisture[1,2] as well as changes in the TGDDM–DDS stoichiometry.[1] The present study examines the influence of these effects on the dynamic mechanical response of this epoxy system at a frequency of 11 Hz in the temperature range of −160 to 320°C. For these experimental conditions, three viscoelastic transitions have been identified. The behavior of these transitions as a function of moisture and stoichiometry provides new insight into the structure of these materials. In addition, by examining the dynamic mechanical properties of a composite film made from the same epoxy system and continuous carbon fibers (Celanese T-300), further elucidation on the nature of these viscoelastic transitions is provided.

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EXPERIMENTAL

Five distinct stoichiometric formulations of the epoxy system considered were studied.   These five formulations were made by mixing approximately 100 parts by weight TGDDM (Ciba-Geigy MY720) with 19, 22, 25, 28, and 31 parts by weight DDS (Ciba-Geigy Eporal).   Since all the formulations were based on 100 parts TGDDM, they will be referred to on parts per hundred basis (phr).   All of the above formulations also contained approximately 11 phr diglycidyl ether of bisphenol A (Celanese SU-8).   Consequently, our system contained the primary constituents of several commercially important resins including the NARMCO 5208 epoxy.[13]   Samples made from these formulations were cast under vacuum from the melt (120°C) into films 0.01 to 0.02 cm thick between stainless steel plates.   The plates were placed in an oven and the temperature was increased from 120–177°C in 30 min.   The films were then allowed to cure at this temperature for 2 hr.   The samples were subsequently stored for two weeks prior to use.

Film samples from the five distinct stoichiometric formulations were then subjected to desiccation and soaking in deionized water for at least a month to ensure that moisture absorption had approached equilibrium.   Moisture determinations were made by drying to constant weight at 110°C and noting the weight loss.   Moisture contents along with the sample stoichiometry are shown in Table I.

In addition to these two levels of water absorption, samples R-1 and R-2 containing 25 phr DDS were subjected to humidities of 52, 88, and 100% as well as boiling in deionized water in order to obtain samples of varying moisture content, as shown in Table II.   It is interesting to note that although these samples were made from different batches of premixed epoxy their moisture uptake was approximately the same.   The unusually high moisture content of the desiccated R-1 and R-2 samples reflects moisture uptake after cure since these samples were not immediately desiccated after the cure was complete, as it was done with all other specimens.

Composite film samples using a unidirectional carbon fiber prepreg tape and an epoxy with 25 phr DDS were also made, resulting in unidirectional composite films 0.01 cm thick with approximately 60% carbon fiber loading.

The dynamic mechanical properties of all the films described above were obtained on strip sample approximately 0.4 cm wide and at least 5 cm long cut from each film by a scratch-and-break technique.   The temperature dependence of the dynamic mechanical properties of these strip samples were obtained in tension with the Rheovibron DDVII which has been modified to prevent sample

TABLE I
Sample Stoichiometry and Moisture Content

Sample	DDS Content, phr	Moisture content, % weight loss	
		Dessiccated	Soaked in deionized water
R-3	19	0.2	4.0
R-5	22	0.2	3.8
R-1, R-2	25	1.3	5.6
R-6	28	0.3	4.7
R-4	31	0.4	4.9

TABLE II
Sample R-1 and R-2 (25 phr DDS) Moisture Content

Treatment	Moisture, % weight loss
Dried at 110°C	0.0
Dessicated	1.3
52% R.H.	3.1
88% R.H.	4.0
100% R.H.	5.0
Soaked in deionized Water	5.6
Boiled in deionized Water	6.4

slippage and moisture condensation on the sample from the environment at low temperatures.[3,4] All experiments were performed at a frequency of 11 Hz and over the temperature range of −160 to 320°C with a heating rate of 1°C/min. The samples in the Rheovibron were maintained in an atmosphere of dry nitrogen. The data obtained were recorded and plotted in the form of the traditional tan δ and dynamic moduli (E' and E'') as well as dynamic compliances (S' and S''). Although only two quantities (E', E'' or S', S'') are sufficient to describe the dynamic mechanical behavior, it has been shown[4,5] that there are distinct differences when the observed transitions in polymers are described by E'', S'', or tan δ. These differences can provide valuable information about the internal stress or strain distribution within the material.

RESULTS AND DISCUSSION

Typical dynamic mechanical spectra for tan δ, E', E'', S', and S'' are given in Figure 1 for a desiccated R-2 (25 phr DDS) sample. From these plots, the three main transitions that were observed for this epoxy system are apparent. In particular, the low-temperature transition centered at −50°C has been identified as the β transition and can be primarily attributed to localized motions of the polymeric chain. The transition centered at about 100°C has been identified as the ω transition and can be attributed to unreacted molecular segments and/or inhomogeneities in the material arising from regions of dissimilar crosslinking densities. Finally, from Figure 1 the high-temperature transition centered approximately at 260°C has been identified as the α transition and can be clearly attributed to the glass transition of the material. Figure 1 also shows that these transitions manifest themselves differently depending on the viscoelastic property under consideration. In particular, one important difference in tan δ, E'', and S'' plots is that the temperature location of the exhibited transition maxima is dependent on the particular quantity being plotted. Although these effects may be of limited significance in developing empirical correlations with moisture and stoichiometry, they become extremely important when correlations with the internal structure of the material is desired. This is a topic that will be addressed in future studies of these materials.

In examining the influence of moisture and stoichiometry on the dynamic mechanical properties of the epoxy samples, no pronounced changes or trends were observed in the storage modulus (E') or storage compliance (S') below 120°C. Variations of ±5% in E' and S' that were observed, can be primarily attributed to variations between batches of the material rather than on moisture
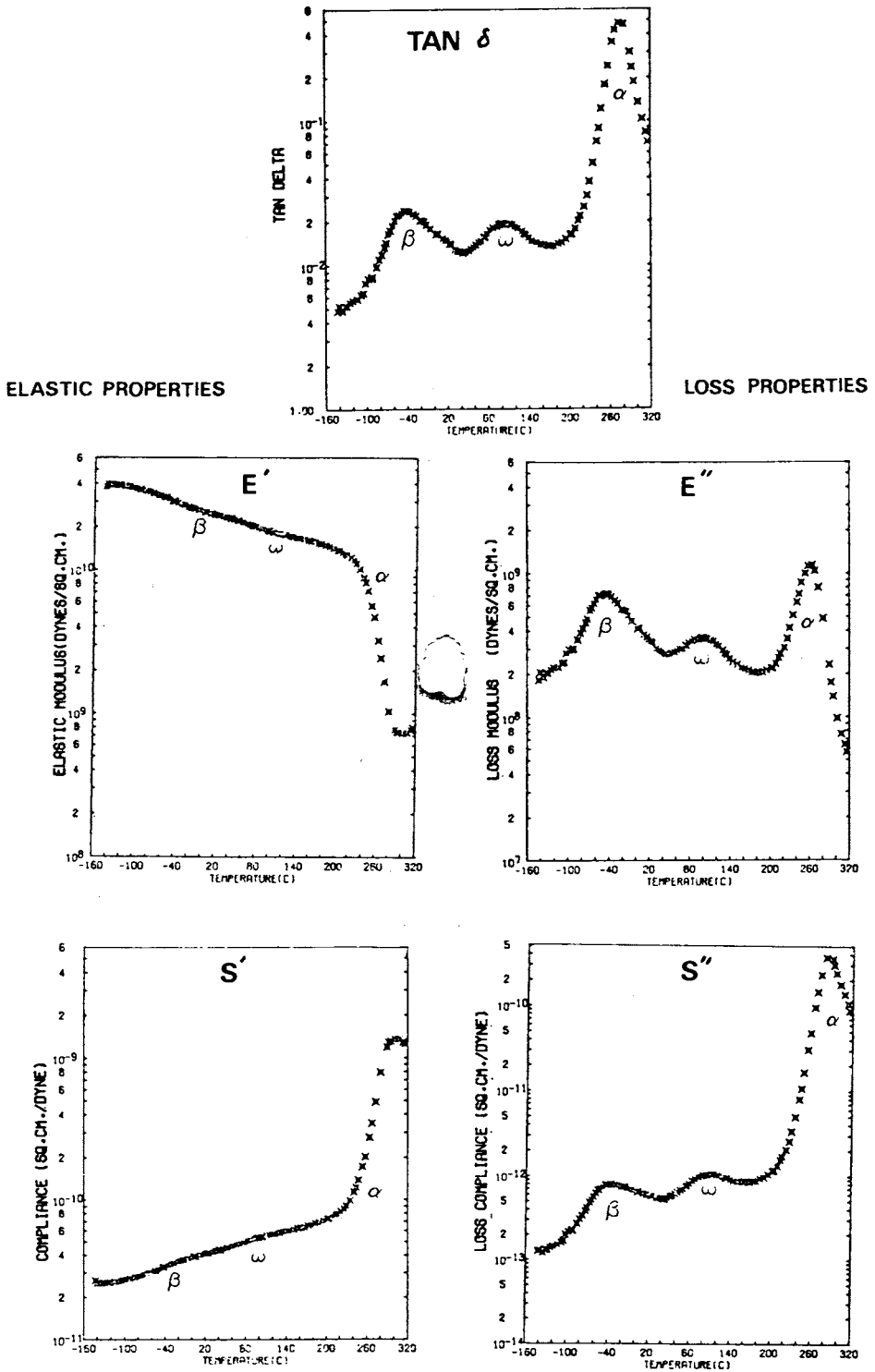
ELASTIC PROPERTIES

LOSS PROPERTIES

Fig. 1. Dynamic mechanical properties as function of temperature for desiccated R-2 (25 phr DDS) sample.

or DDS content. However, pronounced changes in the storage moduli (or compliance) were observed for temperatures higher than 120°C primarily with changes in the DDS composition. This effect is a direct consequence of the influence of stoichiometry at the onset of the glass transition.

α Transition

The insensitivity of the storage modulus to stoichiometry at room temperatures coupled with large changes of the storage modulus at the onset of the glass transition makes it convenient to define the glass transition temperature of these materials as the temperature at which the room temperature (20°C) storage modulus is decreased by half (i.e., $T_g = T_{E'_{RT}/2}$). This definition of T_g has been used by other investigators[1] for the same epoxy system, thus allowing direct comparison with their results. Furthermore, since the room-temperature modulus was approximately equal for all samples examined, this definition of T_g implies that increases in the T_g can be directly associated with increases in the storage modulus (E') past 120°C. It should be emphasized that the glass transition temperature can also be defined in terms of the temperature position of the α peak maximum exhibited in the E'', tan δ, or S'' plots. However, all these definitions of T_g suffer from the fact that they are based on dynamic mechanical quantities which are quite sensitive to the frequency of experimentation as well as the sample heating rate. Consequently, the T_g values defined from dynamic mechanical experiments are invariably higher than the T_g values usually obtained by the more conventional methods (i.e., dilatomeric experiments).

Previous studies[1,2] on the TGDDM–DDS epoxy system have reported that the T_g is reduced by sorbed moisture. Our samples, however, did not exhibit this effect. This lack of T_g dependence on moisture content can be attributed to the fact that the epoxy films examined in this study were thin and tested in a dry nitrogen environment. The fact that T_g for these epoxy films was well above 100°C also contributed in eliminating moisture from our samples by the time T_g was reached. In contrast, our samples did exhibit a strong dependence of T_g on DDS composition, consistent with the results of Morgan and O'Neal.[1] The glass transition temperature of our samples as function of DDS content (in phr) is shown in Figure 2. The corresponding results of Morgan and O'Neal[1] are also shown in Figure 2 for comparison, but it should be recalled that their results were obtained in static experiments; since T_g has been defined in terms of moduli that are strain rate (or frequency) dependent, the discrepancy between results is to be expected. However, it is of interest to note that Morgan and O'Neal[1] found a maximum in T_g of 242°C at 37 phr DDS while our results exhibited a T_g of 247°C at 31 phr. The general increase in T_g with increasing DDS content as shown in Figure 2 suggests increasing molecular weight and/or crosslinking. However, the maximum in T_g observed by Morgan and O'Neal as well as the decreasing slope exhibited by our data in Figure 2 with increasing DDS content supports the contention[1] that unreacted DDS provides a plasticization effect on T_g.

At low concentrations of DDS, an important new effect on the glass transition (α transition) was observed. Samples R-3 (19 phr DDS) and R-5 (22 phr DDS) both exhibited a splitting of the α transition into two separate and distinct transitions which we have defined as α_1 and α_2. Typical results for sample R-5
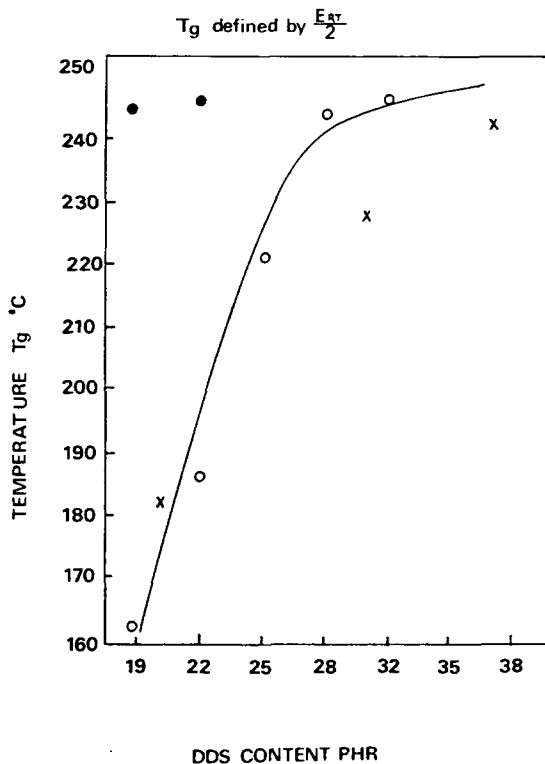
Fig. 2. Glass transition temperature (T_g) of TGDDM–DDS epoxy as a function of DDS content: (O) Primary T_g for each sample; (●) T_g after additional cure for samples that exhibited this behavior; (×) T_g data of Morgan and O'Neal.[1] All T_g's are defined by $E'_{RT}/2$.

(22 phr DDS) are shown in Figure 3(a). The mechanism that we have advanced for this split in the α transition is that additional curing is occurring in these samples. The additional curing becomes evident if we examine the storage modulus (E') and tan δ as a function of temperature for sample R-5 depicted in Figure 3(a). The onset of the glass transition of the sample begins at 120°C, as can be seen by the decrease in E' and increase in tan δ. As the temperature is increased, the material becomes softer as E' continues to decrease along with a corresponding rise in tan δ, indicating increased mobility of the macromolecular chains. However, upon further increase in temperature the modulus E' reaches a minimum at 205°C while the tan δ reaches a maximum at the same temperature, indicating that the material is becoming harder and that the mobility of the macromolecular chains is decreasing. Further increase in temperature produces an increase in E' and a decrease in tan δ, which is indicative of additional cure in the sample.

Consequently, the α_1 transition may be viewed as a composite transition that consists of the glass transition of the original material with the superimposed effect of additional curing. This additional curing, however, is attributable to the increased molecular mobility provided by the onset of the glass transition at a relatively low temperature and is consistent with the fact that the reaction between TGDDM and DDS is steric and diffusion limited.[1] Upon completion
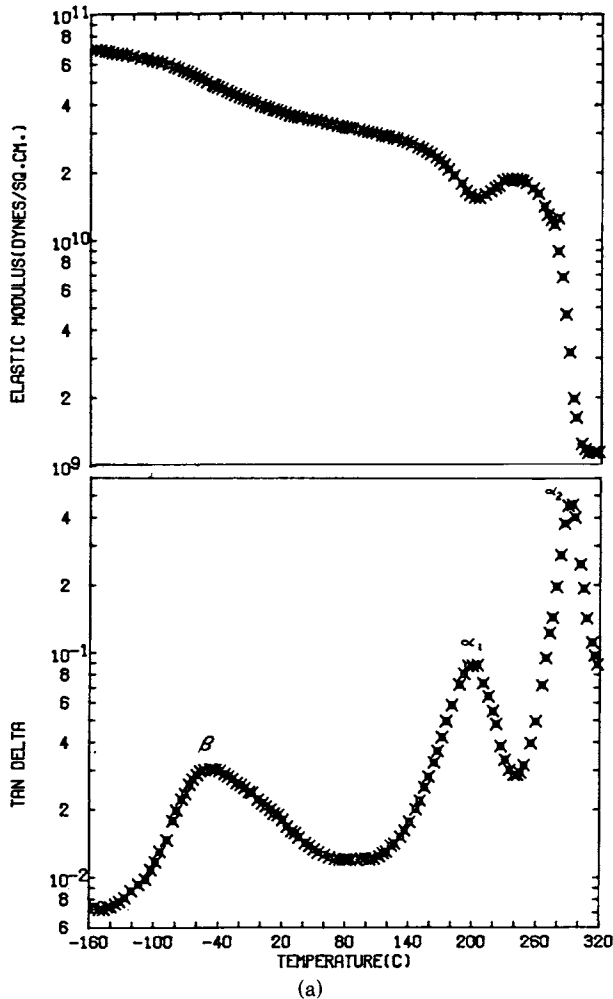
Fig. 3. (a) Dynamic mechanical properties as function of temperature for desiccated R–5 (22 phr DDS) Sample: splitting of the glass transition peak into α_1 and α_2. (b) Dynamic mechanical properties as a function of temperature for desiccated R–3 (19 phr DDS sample: experimental verification of additional cure.

of the additional cure, the E' reaches a maximum at 239°C while the tan δ reaches a minimum. Further increases in temperature again begin to provide increased mobility to the macromolecular chains, which however have undergone additional chain extension and/or crosslinking due to the additional cure. Thus, in effect a new material has been created which in turn proceeds through its glass transition resulting in the appearance of the α_2 transition. It is interesting to note that the temperature location of the α_2 transition is equivalent to the one observed for samples of higher DDS content.

To confirm the proposed additional cure mechanism, sample R-3 (19 phr DDS) underwent dynamic mechanical testing up to the temperature at which its tan δ exhibited a minimum (at approximately 239°C), indicating that the additional cure had been completed. At this point the experiment was stopped and the
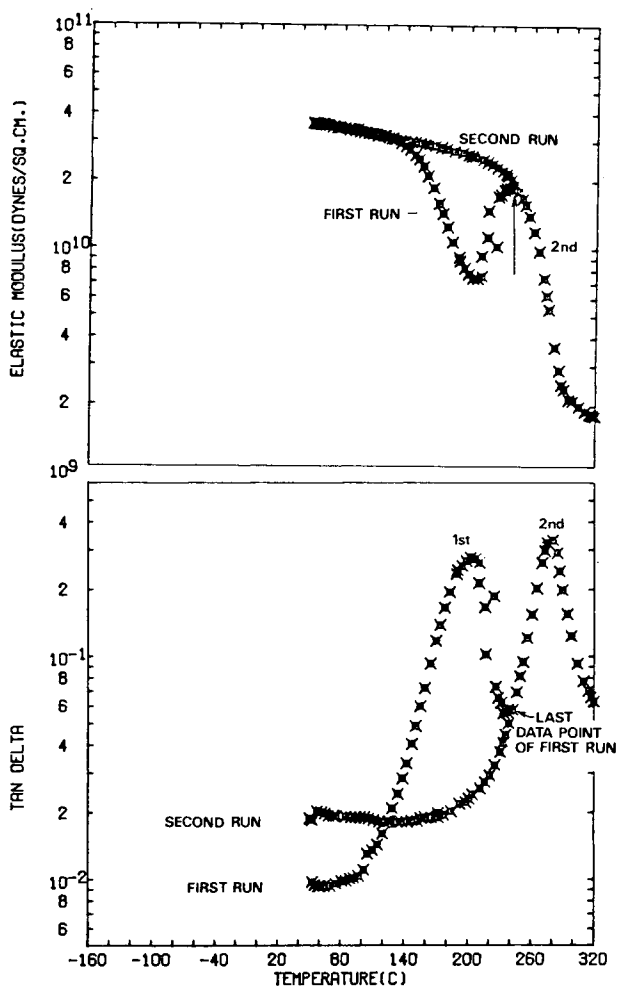
(b)

Fig. 3. (*Continued from previous page*)

sample was allowed to cool to 50°C. Dynamic mechanical testing of the same sample was then repeated up to 320°C. Typical results of these experimental runs for sample R-3 (19 phr DDS) are shown in Figure 3(b). As can be seen, the α_1 transition was not present in the second run, indicating that the sample had gone through an irreversible change due to the additional cure and only one glass transition, α_2, is present. The temperature location of the α_2 transition is also plotted in Figure 2 for samples R-3 (19 phr) and R-5 (22 phr), indicating that the properties of these samples that have gone through additional curing are comparable to samples R-6 (28 phr DDS) and R-4 (31 phr DDS).

Although the above results do not preclude the possibility that additional cure proceeds via a different kinetic mechanism, detailed structural analysis of this system[14] suggests that a single kinetic mechanism which is steric and diffusion limited is responsible for the observed phenomena of additional cure at increased temperature.

β Transitions

In contrast to the α glass transition, which did not exhibit any dependence on moisture content, the β transition centered around $-50°C$ did exhibit a strong dependence on both moisture and DDS content. This β transition, which has been identified in similar epoxy systems,[6-8] can be attributed to a crankshaft rotational motion of the glycidyl portion of the epoxide group in TGDDM after reaction with DDS.[6] The temperature location of the β transition, Figure 4(a), was found to decrease with increasing moisture, which is indicative of the plasticization effect of moisture on the β transition. Although samples prepared with the various amounts of DDS did not shift the temperature location of the β transition to any appreciable extent, either up or down, samples that were prepared with an increasing amount of DDS did exhibit an increasing magnitude of the β transition, as it is shown in terms of tan δ maximum values in Figure 4(b). Thus, it can be assumed that samples prepared with an increasing amount of DDS contain an increasing number of glycidyl groups of TGDDM that have reacted with the DDS. However, these samples with increasing DDS when soaked in deionized water provided an increasing temperature shift to lower
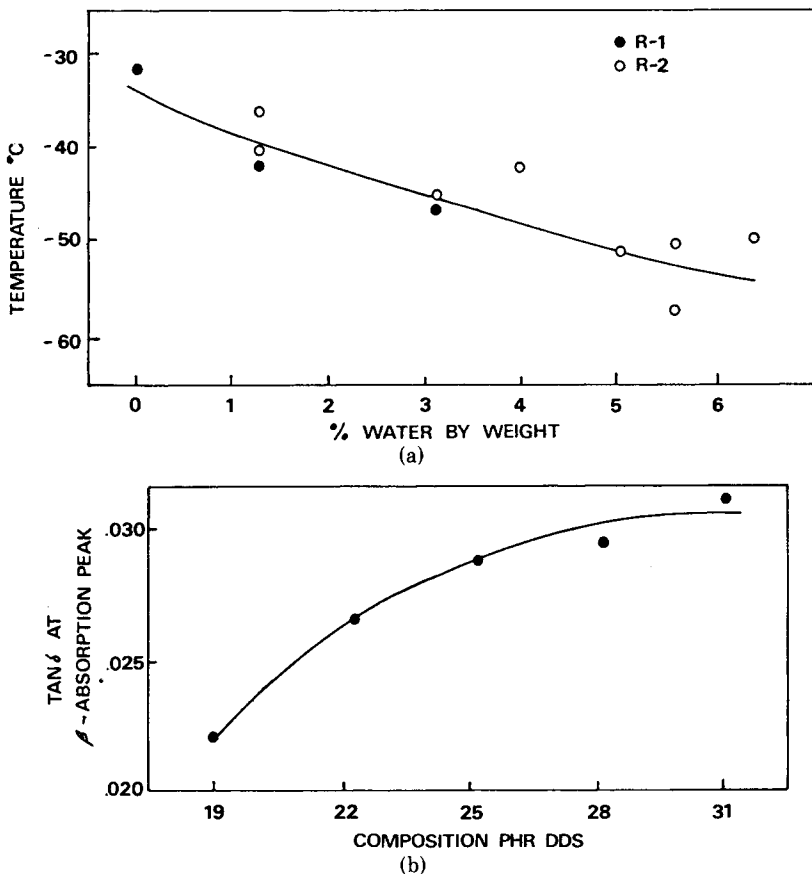

Fig. 4. Influence of stoichiometry and moisture on the β transition. (a) The temperature at which the maximum of the β peak occurs as function of water content for R-1 and R-2 (25 phr DDS) samples. (b) The value of tan δ at the peak position as function of DDS content. (c) The temperature shift of the β transition peak due to soaking ($T = T_{\beta\,desic} - T_{\beta\,soak}$) as function of DDS content.
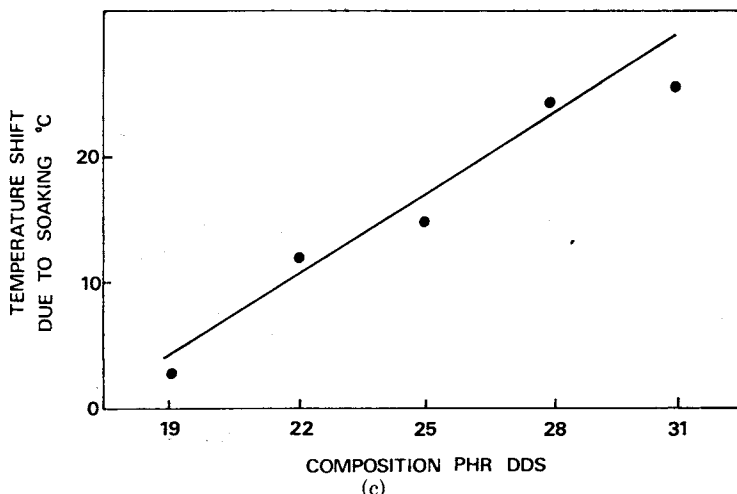
Fig. 4. (*Continued from previous page*)

temperatures for the β transitions, as is also indicated in Figure 4(c). Moreover, not only did all samples exhibit a shift in the β peak to lower temperatures upon soaking, but, in addition, the magnitude of this shift increased with increasing DDS content. The quantitative correlations obtained with moisture and DDS content for the β transition make it particularly attractive as a method for comparing different epoxy systems. Although it represents localized motions of the polymeric chains, the fact that the β transition occurs at low temperatures (below 0°C) guarantees that the sample's internal morphology is preserved during testing and that the changes observed can be directly attributed to that morphology.

ω Transition

The ω transition centered around 100°C also exhibited a dependence on moisture and DDS content, but the effect of moisture was dominant. Figure 5 shows the effects of moisture on tan δ for sample R-2 (25 phr DDS). As can be seen, increasing moisture content not only results in a shift of the ω transition to lower temperatures, but also a noticeable broadening of the ω transition is observed. In addition, the magnitude of tan δ throughout the ω transition, is directly dependent on the moisture content. These effects of moisture on tan δ are similar to results that have been observed when plasticizers of limited miscibility are added to polymeric materials.[9,10] However, in contrast to the β transition, the broadening of the ω transition with moisture content seems to indicate that a distribution of molecular chain segments is involved in the mechanism and supports the contention that moisture is absorbed preferentially in regions of low crosslink densities of the epoxy.[1,2]

Composite Sample

The effect of embedding carbon fibers in the TGDDM–DDS epoxy system as it influences the dynamic mechanical properties is shown in Figure 6. The strip sample tested was cut along the fiber direction of the composite film, and, as expected, the fiber properties clearly dominated. It is interesting to note that throughout the temperature range examined, the value of tan δ has decreased
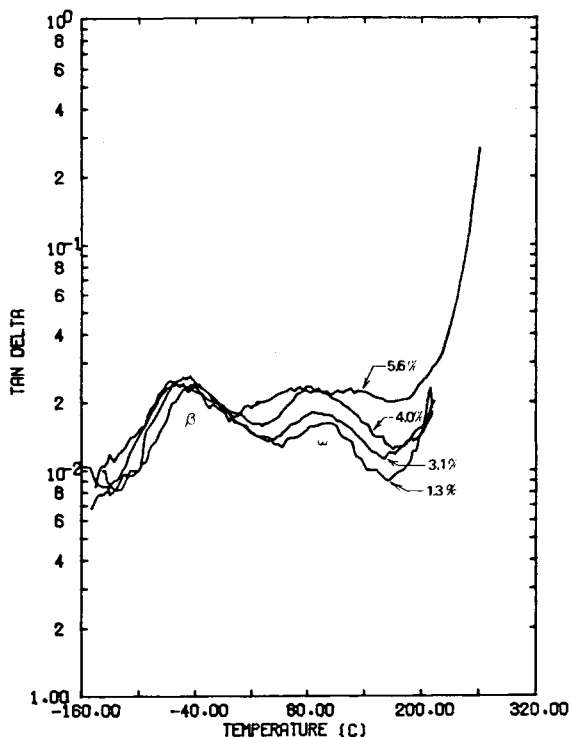
Fig. 5. Tan δ as function of temperature for R-1 (25 phr DDS) samples, demonstrating the effect of moisture on the ω transition. Numbers indicate % moisture content. (Note a reduction in peak temperature as well as the peak broadening with increasing moisture content.)

by an order of magnitude. This high rigidity of the composite film makes questionable the appearance of the low-temperature transitions since operation is carried out at the instrument's limits which contributes to data scatter. However, the appearance of the glass transition is clearly observable. These results, however, also point out that in this epoxy, the β and ω transitions involve localized motions of the polymeric chains while the α transition clearly involves much larger movements of the polymeric chains.

CONCLUSIONS

Three main viscoelastic transitions have been observed for the TGDDM–DDS epoxy system:

(1) The glass transition (α) is strongly influenced by the amount of DDS used in the epoxy preparation and splits into two transitions, α_1 and α_2, for samples prepared with low amounts of DDS. Our results have shown that additional cure in the epoxy system is occurring when splitting of the α transition is observed.

(2) The low-temperature β transition is attributed to a crankshaft motion of the glycidyl portion of the epoxide group in TGDDM after it has reacted with the DDS. Increasing moisture content causes a shift of this transition to lower temperatures, and this shift increases with increasing DDS. Samples prepared with the increasing amounts of DDS exhibited increases in the tan δ at the transition maximum which is consistent with the crankshaft mechanism.
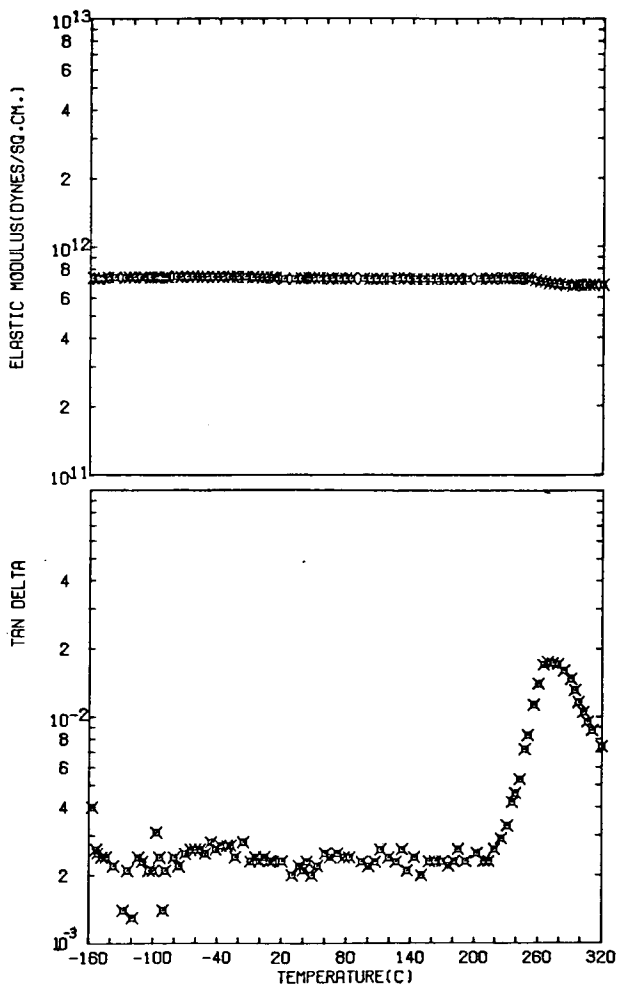
Fig. 6. Dynamic mechanical properties of carbon fiber-reinforced epoxy film.

(3) The ω transition is strongly influenced by the moisture content of the material. Moisture has a strong plasticization effect on this transition, which provides evidence of interaction with regions of low crosslinking density of the material.

The weak or questionable emergence of the β and ω transitions compared with a strong α transition, in the carbon-fiber reinforced epoxy film, further suggests that these transitions involve different portions of the macromolecular chain segments of the epoxy system. The identification and use of these transitions in correlating properties of epoxies and composites made from them can greatly facilitate the manufacture of these materials to meet specific end use properties.

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