Effect of Hygrothermal Fatigue on Dynamic Mechanical Properties of Glass-Reinforced Polyesters

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Synopsis

Several nonreinforced and reinforced crosslinked polyester formulations were prepared and investigated. Solid glass microspheres, with and without coupling agent, were used as reinforcement. All samples were exposed to various cyclic hygrothermal fatigue patterns, differing from one another by the temperature and duration of a cycle. Dynamic mechanical measurements were used to evaluate the effect of hygrothermal fatigue on the mechanical properties of all formulations. Fatigue induced changes in the glass–matrix interphase led to the appearance of relaxation peaks (β' and β'') in the temperature range between $-50°C$ and $-10°C$. Electron microscopic evidence was obtained for the existence of nodular morphology on all fracture surfaces. The character of nodular morphology was described in terms of an inhomogeneous thermoset network.

INTRODUCTION

Glass-fiber- and/or glass-sphere-reinforced polyesters have long been among the most widely used thermoset–matrix composite materials. In actual service, glass-reinforced polyesters are often used in moist environments, and it is therefore of primary concern to evaluate their resistance to moisture. A logical approach would be to expose the material to an aggressive environment which reliably duplicates the actual service conditions. However, impractically long times needed for such tests dictate that the accelerated testing methods be used. The latter typically consist of relatively short cycles during which specimens are exposed to much harsher environmental conditions than those encountered in service. Such cyclic fatigue treatments are projected to be equivalent to a prolonged specimen exposure to milder conditions.

In glass-reinforced polyesters, the elucidation of the effect of water and elevated temperature on the properties of glass–matrix interphase is of utmost importance. Consequently, the interactions between polyester matrix, coupling agent, and glass reinforcement are an area of considerable current research activity. Various high resolution (mostly spectroscopic) experimental techiques have been used to eludicate the nature of interactions in the glass–matrix interphase on the molecular level, and an excellent review of the state-of-the-art of this subject has been recently written by Ishida and Koenig.[1] On the other hand, several reported investigations of mechanical properties of reinforced and nonreinforced thermoset polyesters exposed to moisture have been conducted by comparing dry and wet flexural, tensile, and creep strength.[1-3] However, there have been no reports in the literature on the effect of accelerated hygrothermal fatigue on dynamic mechanical properties of glass reinforced polyesters. Dynamic mechanical analysis offers a distinct advantage over other mechanical property measurements, for it provides the most sensitive response

to various subtle physical and chemical transitions in polymers over a wide temperature range.

The objective of this study is to describe the hygrothermal-fatigue-induced changes in dynamic mechanical properties of various glass-sphere-reinforced polyesters.

EXPERIMENTAL

Polylite (Reichhold Chemicals, Inc.) polyester resin was cured with MEKP (methyl ethyl ketone peroxide, ICN Pharmaceuticals, Inc.). The composition and cure schedule for nonreinforced systems are listed in Table I. Various glass microspheres (Potters Ind., Inc.), used as reinforcement, are described in Table II. The composition and cure schedule for all reinforced systems are also listed in Table II.

A Silastic E RTV (Dow Corning), cured with 10 phr* of Silastic E curing agent,

TABLE I
Nonreinforced Polyester Resin Formulations

Formulation or system no.	Composition	Variable	Cure schedule
1[a]	Polylite 32-037 + 0.5% MEKP	Post-cure time (0–15 hr)	Components mixed at RT for 5 min; vacuum applied for 30 s; poured in silicone molds; 24 h at RT + post-cure at 85°C
1A	Polylite 32-037 + variable % of MEKP	Curing Agent concentration (0.5 → 1.5%)	Components mixed at RT for 5 min; vacuum applied for 30 s; poured in silicone molds; 24 h at RT + 5 h at 85°C

[a] Resin cured for 5 h in the above described cure schedule will be hereafter referred to as formulation 1.

TABLE II
Reinforced Polyester Resin Formulations

Formulation or system no.	Composition	Type of Surface treatment of reinforcement	Cure schedule
2	Polylite 32-037 + 0.5% MEKP + 40% by wt solid glass spheres #3000	No coupling agent	Components mixed at RT for 5 min; vacuum applied for 30 s; poured in silicone molds; 24 h at RT + 5 hr at 85°C
3	Same as 2, Spheres #3000-CP-01	Coupling agent recommended for use with polyesters	Same as 2
4	Same as 2, Spheres #3000-CP-02	Coupling agent not recommended for use with polyesters	Same as 2

was used for the preparation of molds (phr = parts per hundred parts of resin by wt). Each specimen was cast in the mold and cured according to the schedule in either Table I or Table II.

Four fatigue cycles were run, all in water. Each complete cycle lasted 24 h and differed from others by the water temperature during the second stage (7 h) of a cycle. The first and the third stage of a cycle were equivalent in all cases, as described in Table III. Hereafter, the cycles will be referred to by the water temperature during the second stage. All samples were fatigued for 4 and 10 days. Dynamic mechanical (DM) measurements were performed in a DuPont DMA 981 instrument, connected to a 1090 Thermal Analyzer. Tests were run at the oscillation amplitude of 0.2 mm peak-to-peak, and a heating rate of 5°C/min.

One stage carbon–platinum (C—Pt) replicas of fracture surfaces were made and studied by transmission electron microscopy. A CVC CVE-14 evaporator was used for C—Pt replication at pressures of less than 5×10^{-5} torr. Details of the replica preparation procedure are given elsewhere.[4] Samples for scanning electron microscopy were gold shadowed. An AMR-1200 scanning electron microscope and Philips EM 200 transmission electron microscope were used to investigate the fracture surfaces.

RESULTS AND DISCUSSION

Optimum Curing of Pure Polyester—Evaluation of Reference Conditions

Optimum mechanical properties of a cured thermoset are obtained when its glass transition reaches a temperature $(T_{g\infty})$ above which no further curing reactions take place. Such a thermosetting network is then said to be fully cured. There are two molecular phenomena encountered during curing of thermosets: gelation and vitrification. Their significance and interrelation have been nicely discussed in several papers by Gillham.[5] In the case of crosslinked thermosets, it is important to realize that, as long as the temperature of cure (and/or post-cure) remains below $T_{g\infty}$, vitrification will prevent completion of chemical reactions, and such networks will not be "fully cured." Consequently, the $T_{g\infty}$ of an incompletely cured network will depend on the highest temperature achieved during cure (and/or post-cure), and optimum mechanical properties will not be developed. This important fact has often been overlooked or simply left out of many studies of thermosets reported in the literaure.

Consequently, in the first series of experiments, designed to establish a set

TABLE III
Description of Fatigue Cycles

Cycle code	In water (h)		
	2	7	15
RT	−12°C	30°C	30°C
$T_g - 20$	−12°C	59°C	30°C
T_g	−12°C	79°C	30°C
$T_g + 20$	−12°C	99°C	30°C

of reference conditions, post-curing was conducted at various elevated temperatures, and the $T_{g\infty}$ of the system [as defined by the location of loss modulus (E'') peak in dynamic mechanical spectra] was found to be 79°C. In order to develop optimum mechanical properties in fully cured systems, in addition to post-curing at $T \geq T_{g\infty}$, it is imperative to determine a minimum post-curing time needed to reach $T_{g\infty}$. The value of T_g increased during the first 5 h of post-cure and then began to drop. Thence, post-cure time of 5 h was chosen to be optimum and has been used throughout this study. Prolonged post-curing causes a decrease in T_g, most likely due to some degradation of the polymeric network.

In addition to the glass transition (α peak), all dynamic mechanical spectra were characterized by the presence of a low temperature β transition (β relaxation). The molecular origin of β relaxation is believed to lie in the crankshaft motion of most flexible portions of polyester chains incorporated in the thermoset network. No shift in the location of peak of β transition on the temperature scale was observed, although the maximum intensity of the loss modulus β was obtained after the 5-h post-cure. This maximum value indicates the presence of the largest amount of polyester chains incorporated into the thermosetting network upon 5-h post-cure, which is also in agreement with the observed T_g trend as a function of post-cure time. The effect of different amounts of initiator on the location of α and β relaxation peaks was found to be relatively insignificant, and therefore all formulations were cured with 0.5% MEKP.

Nonfatigued Systems

Dynamic mechanical spectra of filled nonfatigued samples, containing coupling agent, show an increase in the value of storage modulus over that of pure polyester. However, Young's modulus of the filled system, not containing the coupling agent (formulation 2), does not differ appreciably from that of pure polyester. Simultaneously, only very slight changes in the value of T_g were noticed between various formulations. Other researchers observed an increase in T_g of filled systems, and attributed it to an absorption phenomenon,[6] although recently it was suggested that T_g can either increase or decrease upon the addition of a filler, depending on the degree of agglomeration of filler particles.[7] In addition, changes have also been observed in the low temperatur region of dynamic mechanical spectra. More specifically, the β relaxation peak shifted from approximately −70°C for pure polyester to about −78°C for filled systems. The filler particles appear to restrictions upon the initiation of crankshaft motion of portions of polyester chains, responsible for the β relaxation.

Fatigued Systems

In Table IV, dynamic mechanical properties of all nonfatigued formulations are summarized and compared to those of fatigued samples exposed to two different fatigue patterns. For all formulations T_g and E' decrease as a function of temperature and duration of a cycle; the relative change in E' being most severe in formulations 2 and 4. However, albeit the values of T_g and E' have decreased, the loss modulus and storage modulus curves of fatigued pure polyester (formulation 1) did not show appreciable qualitative difference from those of nonfatigued samples, as judged by the absence of additional molecular relaxation mechanisms, induced by fatigue.

TABLE IV
Changes in T_g, $T_{\beta''}$, $T_{\beta'}$ and E'_{RT} for Various Systems and Fatigue Patterns

Formula-tion		T_g (°C)	$T_{\beta''}$ (°C)	$T_{\beta'}$ (°C)	$E'_{20°C}$ (GPa)	% decrease in $E'_{20°C}$
1	untreated	79	—	—	3.65	—
	4 days/RT	67.5	—	—	2.60	29
	8 days/60	50	—	—	2.45	33
2	untreated	78	—	—	3.50	—
	4 days/RT	57	−18	−35	2.10	40
	8 days/60	39	−18	−31	1.60	54
3	untreated	79	—	—	4.50	—
	4 days/RT	60	−15 v.weak	—	3.95	12
	8 days/60	54.5	—	−31 broad	2.95	34
4	untreated	78	—	—	4.50	—
	4 days/RT	63	−18	−33	2.80	38
	8 days/60	52	−14	−32	1.90	57

On the other hand, several interesting observations have been made in rein-forced systems exposed to the hygrothermal cyclic fatigue. Systems 2 and 4 (Table II) were investigated first. The most prominent changes in dynamic mechanical properties of these systems have been observed in the temperature region between −50°C and −10°C. One or two additional damping peaks, hereafter referred to as β' and β'', appeared in that temperature range in most samples. For instance, system 2 shows β' and/or β'' peaks whose intensities vary as a function of the duration of cycle and cycle temperature as shown in Figure 1. Whereas no clear distinction could be made between β' and β'' peaks in a broad relaxation region produced upon the RT treatment, the 10-day ($T_g - 20$) cycle is characterized by the appearance of a peak at −35°C (β') and a peak at −18°C (β''). Simultaneously, fatigue induced changes in Young's modulus, as a function of temperature, are shown in Figure 2.
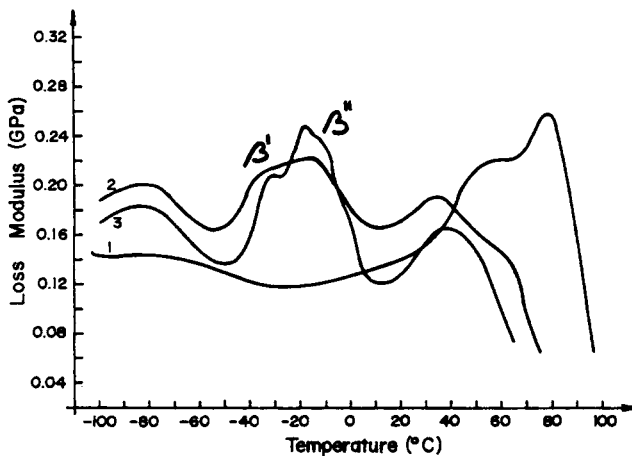

Fig. 1. Loss modulus (E'') as a function of temperature for formulation 2 (without coupling agent); (1) nonfatigued; (2) 4 days/RT; (3) 10 days/($T_g - 20$).
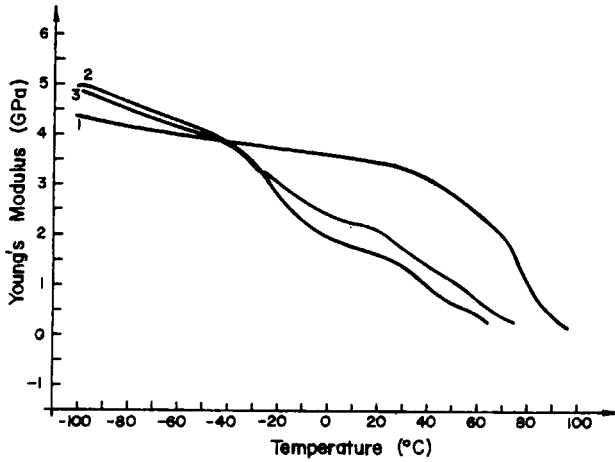
Fig. 2. Young's modulus (E') as a function of temperature for formulation 2 (without coupling agent); (1) nonfatigued, (2) 4 days/RT; (3) 10 days/(T_g − 20).

System 4, which contained coupling agent not recommended by the manufacturer, was characterized by a dynamic mechanical response similar to that of system 2. All fatigued samples, for both 4 and 10 days and at each temperature, had β' and β'' relaxation peaks, as seen in Figure 3. Changes in Young's modulus as a function of temperature for formulation 4, fatigued for 4 and 10 days, respectively, are shown in Figure 4. A rather dramatic decrease in Young's modulus is observed in the β'–β'' relaxation region. On the other hand, in both systems 2 and 4, the low temperature β relaxation was apparently insensitive to cyclic fatigue and the peak value did not appear to shift. This indicates that the crankshaft motion of portions of polyester chains in the thermoset network responsible for the β relaxation is not directly influenced by the fatigue treatment. Albeit the glass transition of the above systems was found to decrease upon fatigue, no exact correlation has been established between the drop in T_g observed in dynamic mechanical spectra, and the fatigue temperature. Fur-
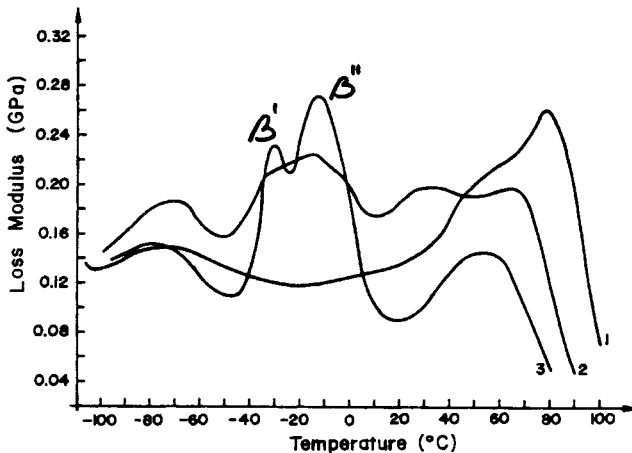

Fig. 3. Loss modulus (E'') as a function of temperature for formulation 4 (with nonrecommended coupling agent); (1) nonfatigued; (2) 4 days/RT; (3) 10 days/(T_g − 20).
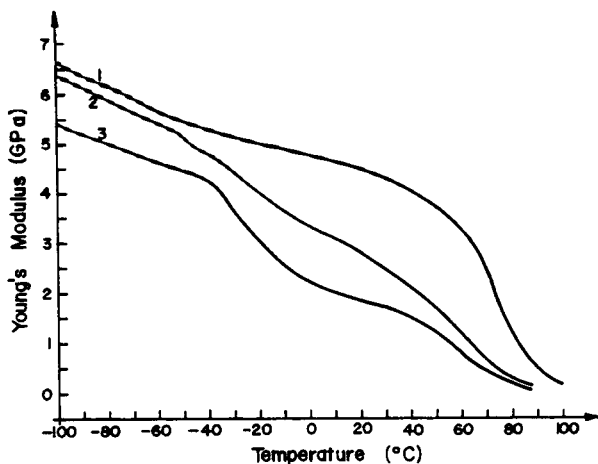
Fig. 4. Young's modulus (E') as a function of temperature for formulation 4 (with nonrecommended coupling agent); (1) nonfatigued; (2) 4 days/RT; (3) 10 days/(T_g − 20).

thermore, judged from the similarity of dynamic mechanical response of systems 2 and 4, it is clear that the coupling agent used in the latter system offers no advantage over the pure beads, at least in conjunction with the polyester resin employed in this study.

β' and/or β'' peaks have not been observed in nonfatigued samples, and thus their presence must be a direct consequence of the hygrothermal treatment. Furthermore, β' and β'' peaks were detected (see Table IV) exclusively in reinforced systems subjected to fatigue, and therefore the locus of the peaks' origin is most likely to be within the glass-matrix interphase. Figure 5 clearly show the appearance of prominent β' and β'' peaks in a filled system (formulation 2) and their absence in pure polyester (formulation 1) after both systems have been exposed to the same fatigue pattern.

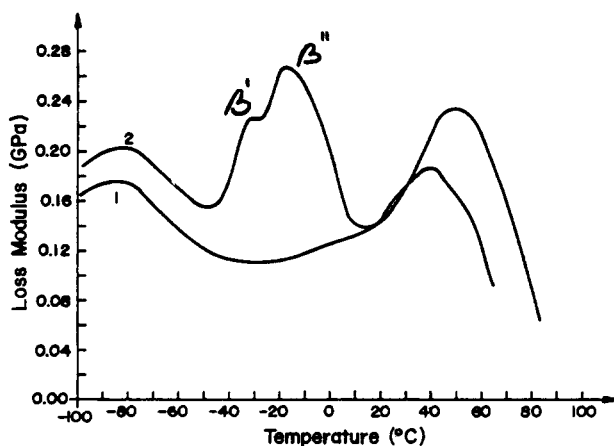In the next series of experiments, system 3 was studied. This system contained

Fig. 5. Loss modulus (E'') as a function of temperature for samples fatigued 10 days in (T_g − 20) cycle; (1) pure polyester (formulation 1); (2) reinforced, but without coupling agent (formulation 2).

the coupling agent recommended by the supplier and was of considerable interest to us as a direct measure of capability of dynamic mechanical techniques to elucidate the effect of hygrothermal fatigue on various glass reinforced formulations. Dynamic mechanical spectra of samples of system 3 show a vary weak response in the $\beta'-\beta''$ relaxation region after a 10-day treatment in $(T_g - 20)$ cycle, as shown in Figure 6. Simultaneous changes in Young's modulus as a function of temperature, for the same fatigue patterns are shown in Figure 7. An abrupt decrease in elastic storage modulus in the $\beta'-\beta''$ relaxation region is not observed in formulation 3. If β' and β'' relaxations peaks are indeed caused by the fatigue induced interactions in the glass–matrix interphase, then the absence of these peaks upon a 4-day exposure to the room temperature and the $(T_g - 20)$ cycles, as seen in Figure 6, indicates the effectiveness of the recommended coupling agent. The latter most likely forms chemical bonds with both glass and resin, which are not susceptible to the attack of water even after 10 days of
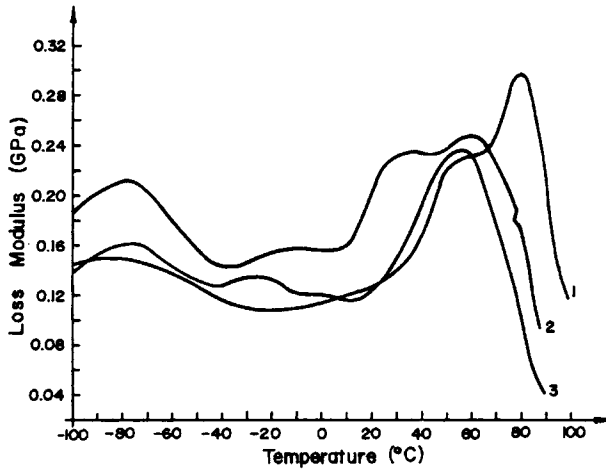

Fig. 6. Loss modulus (E'') as a function of temperature for formulation 3 (with recommended coupling agent); (1) nonfatigued; (2) 4 days/RT; (3) 10 days/$(T_g - 20)$.
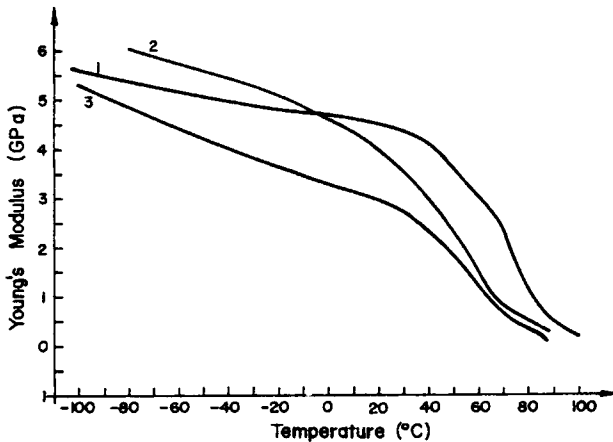

Fig. 7. Young's modulus (E') as a function of temperature for formulation 3 (with recommended coupling agent); (1) nonfatigued; (2) 4 days/RT; (3) 10 days/$(T_g - 20)$.

fatigue in the $(T_g - 20)$ cycle. A drastic difference in the $\beta'-\beta''$ relaxation response of systems with recommended and nonrecommmended coupling agents (formulations 3 and 4, respectively) is clearly depicted in Figure 8. An exposure to higher temperature cycles, however, does have an effect on dynamic mechanical properties of system 3. The T_g cycle upon 10 days and the $(T_g + 20)$ cycle already after 4 days show β' and β'' peaks and a simultaneous drop in T_g, which suggests that after some time at such high temperatures even the interphase containing the recommended coupling agent becomes susceptible to hygrothermal cycling.

In spite of the use of various sophisticated spectroscopic techniques discussed by Ishida and Koenig,[1] a controversy still exists with respect to the exact nature of water-induced changes in reinforced thermosets on the molecular level. It is therefore difficult to define the exact molecular mechanism which causes β' and β'' relaxations. The character of the interphase depends on the type of coupling agent and the nature of coupling agent–glass, and coupling agent–resin interactions. The specific nature of various interactions within the interphase is further complicated by the difference between coefficients of thermal expansions between the polyester matrix and the filler. And perhaps most importantly, a clear understanding of interphase is blurred by recent qualitative observations of morphological gradients.[8-10] The existence of morphological gradients, i.e., variations in resin morphology as a function of distance from reinforcement, implies that different parts of a specimen are characterized by different mechanical properties. For instance, quantitative correlations have been recently established between the size of highly crosslinked inhomogeneities and fracture properties in cured epoxy resins.[11,12] Such relationships are of particular importance in all reinforced systems, where major stress concentration areas occur within the matrix–reinforcement interphase.

To begin with, however, one must understand the fundamental morphology of crosslinked polyesters. An electron microscope investigation of thermoset polyester morphology has not been reported in the literature. Consequently, in the next series of experiments electron microscope studies were conducted
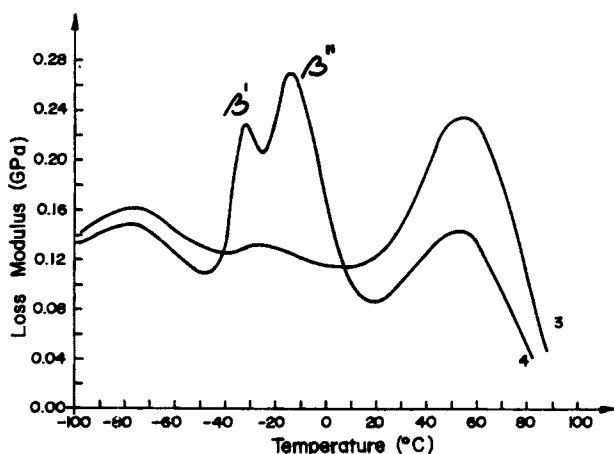

Fig. 8. Loss modulus (E'') as a function of temperature for samples fatigued 10 days in $(T_g - 20)$ cycle; (1) with recommended coupling agent (formulation 3); (2) with non-recommended coupling agent (formulation 4).

to obtain information about the morphological characteristics of all systems. Scanning electron micrographs (SEM) of fracture surfaces of filled systems showed microspheres of various sizes, pronounced in clarity and distributed randomly in the polyester matrix, as shown in Figure 9. Fracture proceeds around the spheres as witnessed by the appearance of either intact spheres embedded in polyester matrix or corresponding holes. Nonetheless, the resolution power of scanning electron microscope is insufficiently high to provide further information about the resin morphology and particularly about the hygrothermal fatigue induced changes within the electron–matrix interphase. On the other hand, transmission electron microscopy (TEM) provides clearer insight into the intricate morphological characteristics of a specimen. Our TEM investigation has clearly shown that a distinct nodular morphology (which did not change as a function of fatigue pattern) characterizes fracture surfaces of all systems. Fracture proceeded around nodules, as clearly seen in TEM micrographs of fracture surface of pure polyester (formulation 1) shown in Figures 10 and 11. The average size of nodules on all samples was approximately 100 nm. It is therefore believed that the morphological model of crosslinked thermoset polyester is best described by the regions of higher crosslink density (nodules) immersed in a lower crosslink density internodular matrix. A similar qualitative suggestion has been schematically described by Dombroski.[13] That nodules are indeed sites of higher crosslink density has been shown in Figures 10 and 11 by the fracture proceeding around nodules. Analogous observations have been previously made on various epoxy resins. A chronological development of the entire concept of inhomogeneous thermoset morphology has been considered at length elsewhere.[11] Although it is now generally accepted that the more highly crosslinked nodules (ranging in size from 6 nm to 10 μm), surrounded by a lower molecular weight matrix, represent the morphology of various thermosets, our micrographs are the first such evidence for crosslinked polyesters. Nevertheless, the inability to differentiate nodular and internodular regions by some common
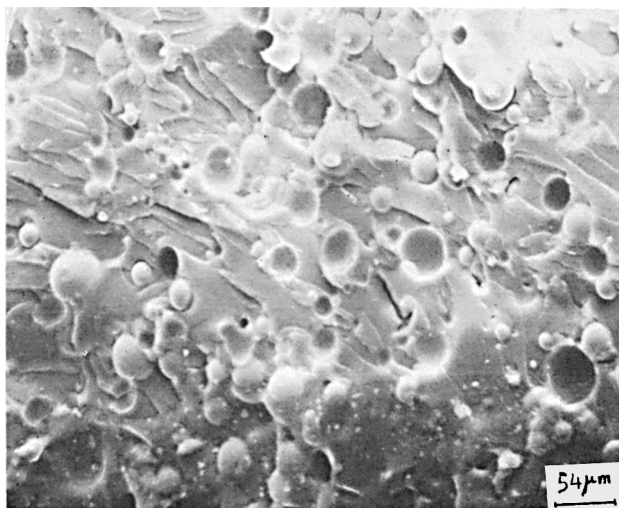

Fig. 9. Scanning electron micrograph of a fracture surface of glass microsphere reinforced polyester resin (formulation 3, Table II). Sample was fatigued for 4 days in $(T_g - 20)$ cycle. Tilt angle 32°.
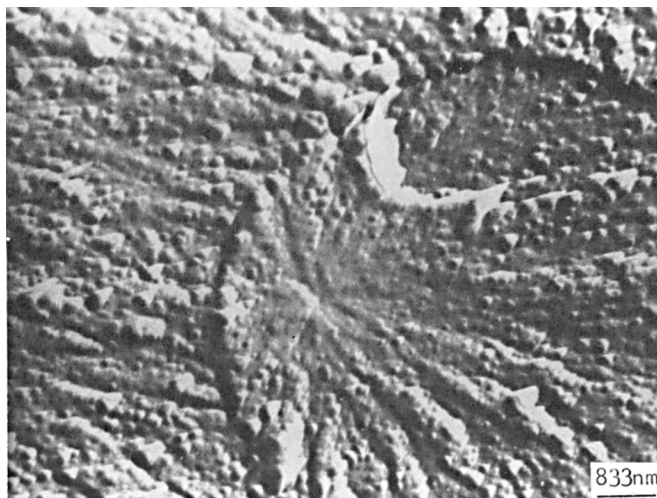
Fig. 10. Transmission electron micrograph of a one stage C—Pt replica of fracture surface of pure polyester (formulation 1) fatigued for 10 days in $(T_g - 20)$ cycle. Note characteristic nodular morphology.

experimental techniques, such as small-angle X-ray scattering, has cast doubts about the existence of nodules. It is believed, however, that this inability is a direct consequence of a very small electron-density difference between the more highly crosslinked nodules and the internodular matrix. Likewise, dynamic mechanical measurements of crosslinked thermosets generally show a single glass transition because the onset of molecular motion in nodules and internodular regions occurs over a rather narrow temperature range. If an experimental technique is to distinguish between these two regions, one must accentuate the difference between the nodules and the internodular matrix by causing changes
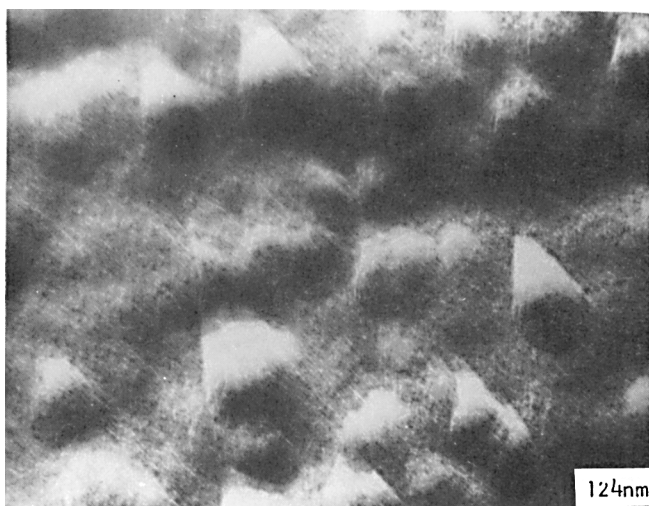

Fig. 11. Transmission electron micrograph of a one stage C—Pt replica of fracture surface of pure polyester (formulation 1) fatigued for 10 days in $(T_g - 20)$ cycle. Note characteristic nodular morphology.
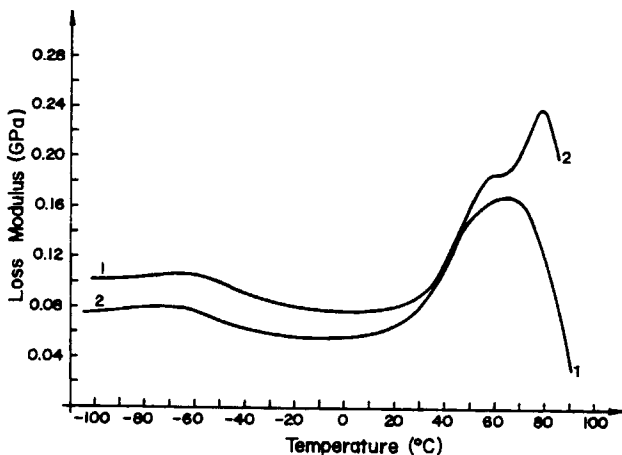
Fig. 12. Loss modulus (E'') as a function of temperature for formulation 1 (nonfatigued pure polyester); (1) 24 h after the completion of curing cycle; (2) after 60 days of annealing at 25°C.

in one region, while the other remains intact. For instance, a preferential swelling of the less highly crosslinked internodular region would presumably lower its glass transition enough so that the dynamic mechanical spectra would show two α peaks, one due to the swollen internodular matrix and the other due to nodules. An attempt to characterize network morphology of an epoxy resin by a combination of dynamic mechanical and swelling tests has been reported.[14] We have used an annealing technqiue to differentiate between the nodular and internodular regions. It is a well-known fact that annealing of polymeric materials causes various processes of reorganization of polymer morphology. For instance, annealing can relieve frozen-in stress and/or induce additional crystallization in semicrystalline polymers. Annealing is usually done in the vicinity of polymer glass transition, for a relatively short period of time. In this study, however, annealing was carried out in air, at 25°C for 60 days. Upon annealing, two peaks
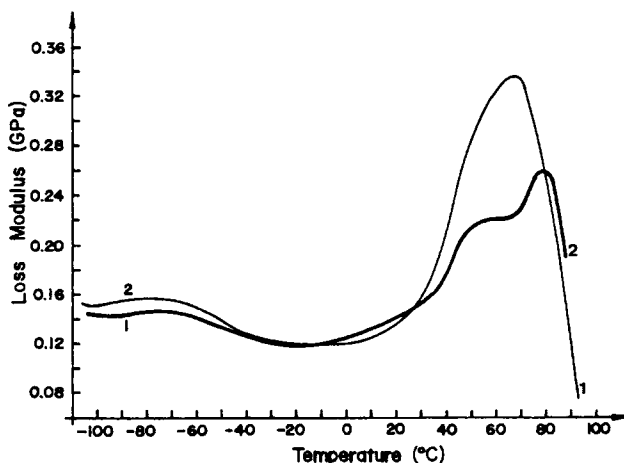

Fig. 13. Loss modulus (E'') as a function of temperature for formulation 2 (nonfatigued, without coupling agent); (1) 24 h after the completion of curing cycle; (2) after 60 days of annealing at 25°C.

were observed in the T_g region of neat and reinforced samples, as clearly seen in Figures 12 and 13, respectively. The lower of these peaks was below, and the higher one above the single α peak recorded in nonannealed specimens. Similar observations have been reported first by Kreibich and Schmid.[15] These authors have observed two α peaks in DSC thermograms of an epoxy system, already after 70 h of annealing at temperature well below the $T_{g\infty}$. We believe that, due to a less restricted chain mobility in the internodular matrix, a partial rearrangement (ordering) of polymeric chains takes place. Such molecular motions occur in the solid state and thence very slowly. Therefore, long annealing times are necessary to rearrange (order) enough segments in the internodular regions, which, in turn, would give rise to a separate α peak in dynamic mechanical measurements. When an annealed sample is heated during dynamic mechanical testing, it first reaches the onset of molecular motion of partially rearranged (ordered) chains in the internodular region. Since nodules are characterized by higher crosslink density, a higher temperature is needed to entice the molecular motion within nodules. Consequently, the second peak signifies the onset of molecular motion within nodules. Once the testing temperature exceeds the glass transition of annealed internodular region, the partial rearrangement (order), produced during annealing is lost and random chain configuration reappears. If such sample is then retested, at 5°C/min starting at low temperature, only one relatively broad α peak appears.

To summarize, the results of our investigation are consistent with the model of higher crosslink density nodules immersed in a lower-crosslink-density internodular matrix. On the other hand, our dynamic mechanical measurements have shown that hygrothermal fatigue induces molecular relaxations in the glass–matrix interphase. Therefore, an accurate explanation of fatigue-induced molecular mechanisms in the interphase requires the knowledge of morphological gradients. This problem is currently being researched in our laboratories.

CONCLUSIONS

The effect of hygrothermal fatigue upon dynamic mechanical properties of various reinforced thermosetting polyesters was evaluated. The glass transition and elastic modulus of each formulation were shown to decrease as a function of temperature and duration of a fatigue cycle. In all reinforced systems hygrothermal fatigue was found to induce changes in the glass–matrix interphase. Such fatigue induced changes were characterized by the appearance of β' and β'' relaxation peaks in the temperature region between $-50°C$ and $-10°C$. Intensities of those peaks vary as a function of temperature and duration of a cycle, although the exact molecular mechanism responsible for their appearance is not known. Nonetheless, changes in dynamic mechanical properties in the $\beta'-\beta''$ region can be used as a direct measure of decrease in elastic modulus and a measure of the effectiveness of coupling agent. The evidence from electron microscopic studies and annealing experiments is consistent with the morphological model of higher-crosslink-density nodules immersed in a lower-crosslink-density matrix.

References

1. H. Ishida and J. L. Koenig, *Polym. Eng. Sci.*, **18**(2), 128 (1978).

2. O. K. Johanson, F. O. Stark, G. E. Vogel, and R. M. Fleishmann, *J. Composite Mater.*, **1**, 278 (1967).

3. K. H. Ashbee and R. C. Wyatt, *Proc. Roy. Soc.*, **A312**, 553 (1969).

4. J. Mijović and J. A. Koutsky, *J. Appl. Polym. Sci.*, **23**(4), 1037 (1979).

5. J. K. Gillham, *Polym. Eng. Sci.*, **19**(10), 676 (1979).

6. D. H. Droste and A. T. DiBenedetto, *J. Appl. Polym. Sci.*, **13**, 2149 (1969).

7. B. L. Lee and L. E. Nielsen, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 683 (1977).

8. R. E. Cuthrell, *J. Appl. Polym. Sci.*, **12**, 955 (1968).

9. J. L. Kardos, *Trans N.Y. Acad. Sci. II*, **35**(2), 136 (1973).

10. J. L. Racich, Ph.D. dissertation, University of Wisconsin-Madison, 1977.

11. J. Mijović and J. A. Koutsky, *Polymer*, **20**, 1095 (1979).

12. J. Mijović and L. Tsay, *Polymer*, **22**, 902 (1981).

13. J. R. Dombroski, SPI 31st Annual Technological Conference, 1976, Sec. 14B, pp. 1–5.

14. A. S. Kenyon and L. E. Nielsen, *J. Macromol. Sci., Chem.*, **A3**(2), 275 (1969).

15. T. T. Kreibich and R. J. Schmid, *J. Polym. Sci., Polym. Symp.*, **53**, 177 (1975).