Thermally Stimulated Creep (TSCr) Study of Viscoelastic Behavior and Physical Aging of a Polymeric Matrix Composite for Spacecraft Structures

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Received 15 July 2001; accepted 8 October 2001

ABSTRACT: Thermally Stimulated Creep (TSCr) mechanical spectroscopy has been used to analyze molecular movements in KMU-4*l*carbon/epoxy composite material around the glass transition temperature. This technique is powerful to characterize the microstructure and micromechanical properties of the epoxy matrix and their evolution upon thermal aging. Three cooperative submodes have been distinguished by resolving the fine structure of the material complex α-retardation mode. The elementary processes constituting this mode possess activation enthalpies and preexponential factors that strongly depend on the thermal history of the sample. The activation parameters of the composite are subject to perceptible evolution due to postcuring degradation. The α-mode associated complex spectrum shifts towards higher temperatures by 27°C as a consequence of a series of quenching in the temperature range 260 to 0°C; the material shows a rise in the fragility and a deterioration in the crack-growth resistance qualities.
 J Appl Polym Sci 85: 342–350, 2002

Key words: ageing; composites; creep; microstructure; viscoelastic properties

INTRODUCTION

Numerous researches have shown that materials and structures of any long-life spacecraft are disposed to thermal aging, which is still investigated in many in-space and laboratory experiments. Thermal cycling takes place in a real low Earth orbit space environment because each orbit (about 90 min) the spacecraft is alternatively lit by Sun and shaded by Earth. The extreme temperatures are thought to be −150 to +150°C; however, actually they are between these extreme values. For example, the space station "Mir" during 15.1 years of operation has acquired more than 85,000 thermal cycles with an amplitude of [−80°C, +130°C]. The effects caused by thermal cycling in space should be studied carefully because they are probably responsible for irreversible degradation (delamitation, bulk microcracking, and dimensional properties alteration) of spacecraft materials and structures such as solar cell arrays, load-bearing units, and micrometeoroids protection skin.[1–4]

Thermal aging of polymeric matrix composites involves chemical and physical transformations. A better knowledge of the molecular mobility in epoxies and information on the thermal mechanical behavior and physical aging of composite ma-

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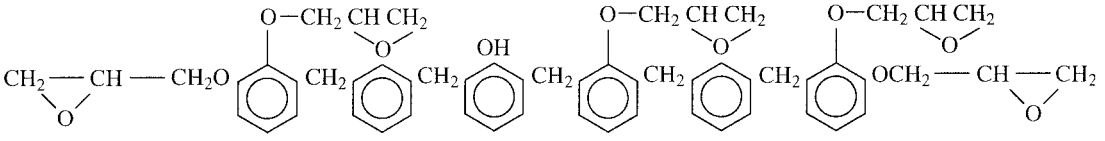
Journal of Applied Polymer Science, Vol. 85, 342–350 (2002)

terials are necessary to understand damage accumulation mechanisms as well as to develop epoxy matrices and new composite materials with improved properties. Different thermal methods like Dynamic Mechanical Analysis (DMA), linear dilatometry, Differential Scanning Calorimetry (DSC), dynamic mechanical spectroscopy are used in experimental studies of composites. Particular attention should be paid to TSCr techniques, which permit broad retardation modes peculiar to polymeric matrices and composite materials to be resolved into a set of elementary processes characterized by their retardation times.[5–7] The viscoelastic behavior of the material (mechanical loss compliance) can be derived from TSCr spectra by simple calculation. We applied the TSCr approach to observe thermal evolution of the microstructure and molecular mobility of one commercially available carbon/epoxy composite.

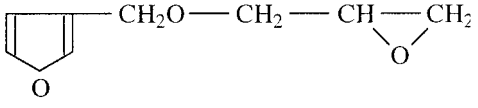
MATERIALS AND METHODS

Materials

The experimental material is a modern highly rigid KMU-4*l* (0°/90°) laminated composite applied in structures of "Mir"-type space stations. KMU-4*l* composite was developed at the All-Russian Institute of Aviation Materials (Moscow).[8] It consists of nine alternating layers of the matrix and LU-3 reinforcing carbon tape. The thickness of these layers is 0.17–0.20 mm and 0.13–0.15 mm, respectively. The material contains ENFB epoxy matrix, the basic components of which are EN-6 high-strength heat-resistant resin:



and furfurylglycidylic ether (the major hardener):



EN-6 benzylamine complex of boron fluoride has six phenyl groups and represents nitrogenated products of the polycondensation reaction of epichlorohydrin with phenolformaldehyde resin. As opposed to other epoxy matrices cured by amines, anhydrides, or phenol-formaldehyde oligomers, ENFB matrix is cured with a boron trifluoride curing agent BF_3 (4% of the final total mass constitution). These basic components are loaded into an autoclave with an organic degreasing solvent (ethyl alcohol or acetone) in a proportion of 2/3, and cured according to the catalytic mechanism.

The chemical composition determines the network molecular structure and main advantages of this matrix in comparison with the traditional 5-211B epoxy matrix[8] (improved stress–strain properties (compression and flexure elasticity modulus, strength parallel and perpendicular to the fiber, high crack-resistance, and glass transition temperature). Materials on the basis of ENFB matrix possess high chemical and thermal stability combined with low coefficient of thermal expansion.

Methods

Thermally Stimulated Creep

The TSCr experimental procedure is fully described in ref. 9. To register complex spectra of the investigated material, a static shear stress σ = 145 MPa was applied to the sample at a load temperature T_σ for 2 min to allow mobile groups to orient and the viscoelastic strain γ to establish. Upon quenching the sample to T_o = 0°C the stress was removed and the normalized rate of deformation $|\dot{\gamma}/\sigma|$ representing the complex TSCr spectrum was measured warming the sample up to 260°C with a temperature rate of 5°C/min, which induces a return to equilibrium of the system. The difference $T_\sigma - T_o$ is called the stress temperature window. This spectrum corresponds to the high-temperature relaxation mode, and can be associated with the viscoelastic manifestation of T_g.

According to the TSCr principle, a complex retardation mode can be resolved into a set of elementary monokinetic processes[9] To register elementary spectra of the material one should per-

form an experimental procedure known as the fractional loading technique. Its methodology is similar to the described one but the stress temperature window $T_{1\sigma} - T_{2\sigma}$ is usually taken as 5°C, and it is shifted by 5–10°C from 0 to 260°C. Thus, we observe a series of elementary spectra of the epoxy matrix composite.

Each fractional loading response $|\dot{\gamma}/\sigma|$ is characterized by its single retardation time $\tau_i(T)$ and activation enthalpy ΔH_i. The retardation time is calculated as a function of temperature:

$$\tau_i(T) = \left| \frac{\gamma_i(T)}{\dot{\gamma}_i(T)} \right|, \quad (1)$$

where γ_i is the deformation for the i process, $\dot{\gamma}_i(T)$ is the rate of change of γ of the i process. The temperature dependence of the $\tau_i(T)$ is generally well described by the Arrhenius equation

$$\tau_i(T) = \tau_{0i} \exp \frac{\Delta H_i}{RT}, \quad (2)$$

where R is the universal gas constant, τ_{oi} is the preexponential factor, ΔH_i is the activation enthalpy. Then the single retardation time τ_i is represented on the Arrhenius diagram as a function of reciprocal temperature $1/T$ (K^{-1}). Experimental points on the plot of log τ_{oi} vs. ΔH_i often follow a straight line. In this case, the retardation times of the processes constituting the retardation mode obey a compensation law

$$\tau_i(T) = \tau_c \exp\left\{ \frac{\Delta H_i}{R} (T^{-1} - T_c^{-1}) \right\}, \quad (3)$$

where the compensation temperature T_c and the compensation time τ_c are constants. This behavior reflects cooperative molecular mobility according to a series of data on polymeric materials.[5–7] The described analytical procedure was performed on the whole series of TSCr spectra to observe evolution of the activation and compensation parameters in KMU-4*l* carbon/epoxy composite subjected to repeated thermal treatments. The results are presented and discussed in the next section.

Dynamic Mechanical Analysis

The method of DMA was employed to measure the complex shear modulus $G^* = G' + iG''$, bending modulus M', and mechanical loss tangent tan δ in the temperature interval ranged between 20 and 270°C. The G' modulus was measured using the reversible torsion pendulum at a frequency of 1 Hz.[10] The incertitude is about 3%. Three repeated DMA scans performed on the same samples permitted to estimate the α-relaxation temperature T_α determined from the maximum of the variation of tan δ vs. temperature or from the minimum of the first derivative dG'/dT.

To raise the reliability of the analysis, a new approach was suggested in ref. 3 for processing and analyzing the temperature-dependent mechanical properties measured on DMA. It consists in resolution of the tan $\delta(T)$ complex peak and the first derivative dG'/dT in the α-transition region of the matrix into a set of Gaussian elementary processes. Such a choice of the base function is dictated by the fact that relaxation units in heterogeneous media conform to the Gaussian normal distribution.

According to principles of the dynamic mechanical spectrometry, smoothed dependence of the dynamic shear modulus $f_k(T_k)$ is derived and the first derivative $\partial f_k/\partial T_k$ is resolved:

$$f_k = \sum_{j=1}^{m} g_{jk},\ g_{jk} = a_j \exp\left\{ -\ln(2) \frac{(b_j - T_k)^2}{c_j^2} \right\}, \quad (4)$$

where $k = 2, \ldots, n - 1$, n is the number of experimental points, a_j is the intensity of the j peak, b_j is abscissa of the central point of the j peak, c_j is the half-width of the j peak, T_k is the temperature, m is the number of Gaussian peaks.

In general, in view of the molecular mobility origin of the matrix, the α-transition region represents a superposition of several overlapped molecular processes located in regions of the matrix ordered with different rates. Within this conception, each Gaussian peak corresponds to a molecular process that reveals itself under specific thermophysical conditions. Several numerical criteria for determining the matrix characteristic temperatures on the basis of parameters of Gaussian processes (temperature position, half-width and intensity of peaks) can be proposed.[3]

RESULTS AND DISCUSSION

TSCr and DMA Complex Spectra

Preliminary TSCr measurements showed that temperature maximum of the complex spectrum

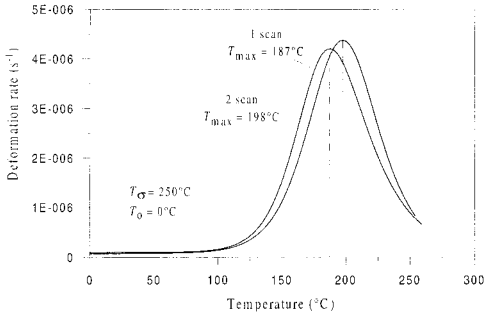


Figure 1 Complex TSCr spectra of a preliminary dried sample of KMU-4*l* composite. A shift of 11°C is detected in the spectrum temperature position measured in two successive scans.

significantly depends on the loading temperature T_σ. The optimum loading temperature $T_{\sigma\ \text{opt.}}$ turned out to be located 45°C higher than the material glass transition temperature T_g. Note that the T_g of KMU-4*l* composite measured on MDSC 2920 setup is 205 ± 3°C. Thus, Figure 1 represents TSCr complex spectra obtained in two successive scans in a temperature range of 0 to 260°C according to the above-described protocol with application of the shear stress at a loading temperature T = 250°C. These spectra correspond to the high-temperature retardation mode and can be associated with the glass transition in the polymeric matrix composite.

The maximum of the TSCr complex spectrum of preliminary dried samples of KMU-4*l* in the initial state is at $T_{\alpha\ \text{TSCr}}$ = 187°C (Fig. 1). It was found that the complex spectrum shifts by several degrees towards higher temperatures with each TSCr scan due to thermal aging of the sample being measured (postcuring effects like crosslinking). These effects have been discovered earlier and estimated in numerous independent experiments with carbon-reinforced and glass-reinforced epoxy laminates after long-term exposure to thermal cycling on the surface of the space stations "Salyut," "Mir," and LDEF.2,3 One can ascertain that the postcuring degree depends upon the properties of the epoxy matrix and the temperature of the surface when the material is lit by the Sun.

Therefore, the thermal cycling is the major factor responsible for increase of the α-relaxation temperature $T_{\alpha\ \text{DMA}}$ of composite materials in space station structures. The postcuring is detected in Figure 2(a) and (b) by the shift of the tan δ peaks and the regions of decrease of the modulus G' of KMU-4*l* composite material subjected to prolonged thermal cycling during 839 and 1218 days of space exposure at "Mir" station. Computer analysis of DMA data performed according to principles of the dynamic mechanical spectrometry[3] has allowed analytical resolution of the complex α-relaxation mode into a set of Gaussian elementary processes. It can be established [Fig. 2(c)–(f)] that the postcuring process is accompanied by not only a rise in T_α but also by evolution of the fine structure of the region of the vitreous state of the epoxy matrix. The comparative study points out that the magnitude of the composite postcuring degree depends for the most part on the amount of thermal cycles obtained by the material in space. Nevertheless, the sensitivity of the DMA seems to be insufficient, which limits potentialities of the spectrometric processing in reliable disclosure of the fine structure of DMA complex spectra in the region of the α-relaxation mode.

The rate of change of the α-relaxation temperature $T_{\alpha\ \text{DMA}}$ for KMU-4*l* composite exposed to the space environment over six periods of time is represented in Figure 3. It is evident that the postcuring effect predominates over destruction processes because long-term influence of space factors has never resulted in a decrease of T_α. The effects related to physical and chemical transformations in the matrix finish within 800–1200 days, and the composite material attains stable properties.

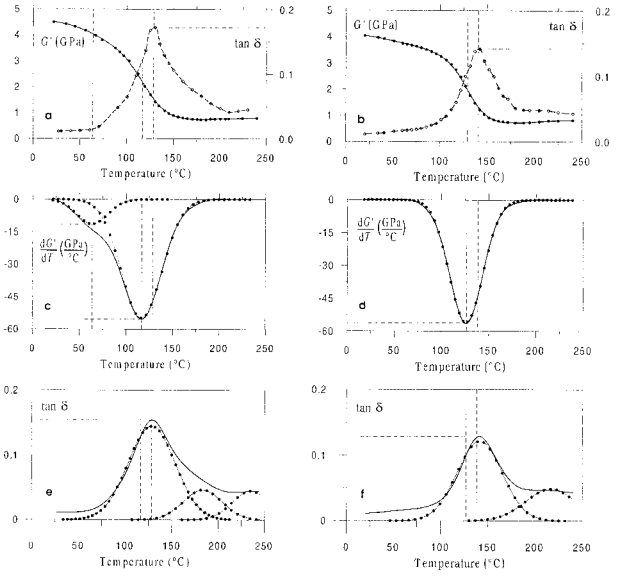


Figure 2 Numerical analysis (c)–(f) of DMA measurements (a,b) of KMU-4*l* composite material after 839 and 1218 days of exposure to the space environment at "Mir" station.

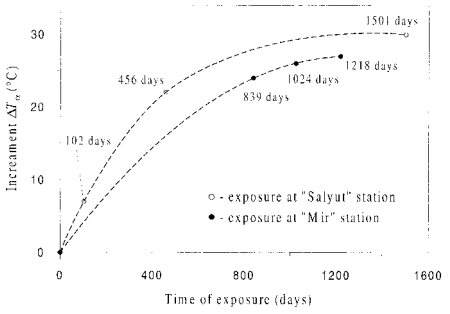


Figure 3 Magnitude of the postcuring process in the epoxy matrix of KMU-4*l* composite material as a function of the time of space exposure.

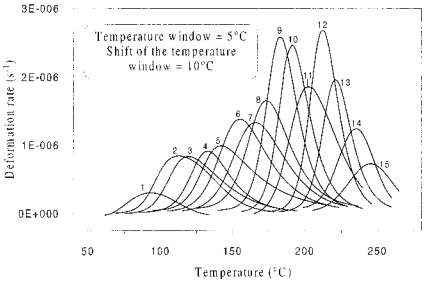


Figure 4 TSCr elementary spectra of KMU-4*l* composite in the region of α-relaxation measured with a shift of the stress temperature window of 10°C (weak aging).

It should be noted that the exposure conditions are not stationary over the time of exposure abroad a space station. This instability along with the nature of synergistic influence of space factors upon structural materials can be responsible for the noticeable distinction in the behavior of ΔT_α inherent to KMU-4*l* composite if one compares the magnitude of postcuring effects in two series of samples exposed at "Salyut" and "Mir" space stations (Fig. 3).

Elementary TSCr Spectra

To investigate the glassy into rubbery state transition, the fractional loading procedure was applied in the whole temperature range of the corresponding complex spectrum of the material. TSCr elementary spectra were recorded on three different samples with shifts of the temperature window of 5, 10, and 15°C. Therefore, each sample can be characterized by its thermal history, and can be conventionally referred as a sample undergone weak or strong thermal aging.

Typical examples of elementary spectra in KMU-4*l* measured on two different samples with shifts of the stress temperature window of 10 and 5°C are shown in Figures 4 and 5. The distribution of the activation enthalpies in KMU-4*l* composite as a function of the peak i maximum temperature T_{m_i} can be seen in Tables I and II, and in Figure 6. The activation enthalpies ΔH_i calculated from the Arrhenius model (2) vary from 150 to 385 kJ/mol. From nearly 160°C the activation enthalpy increases gradually with temperature and then decreases as soon as the material gets into the rubbery state. The profile of $\Delta H_i(T_{m_i})$, compared to other TSCr measurements (Fig. 6), strongly depends on the thermal history of the considered sample.

This study has been completed by analyzing the distinction of the molecular mobility in ENFB epoxy matrix in comparison to other conventional polymeric matrices.[8] With the cooperative high-temperature mode, we are dealing with movement that propagates along the chain. According to Hoffman, Williams, and Passaglia,11 the larger the activation enthalpy distribution, the larger the mobile unit. The broad range of the activation enthalpies ΔH_i indicates that long rigid segments are present in the matrix and their molecular processes constituting the α-retardation mode are highly delocalized. Raising of the temperature above the T_g value provokes further liberation of molecular movements around the glass transition temperature of the matrix that creates favorable conditions for the progress of postcuring effects responsible for physical aging of the material. The molecular mechanisms of these effects naturally involve evolution of the microstructure and micromechanical parameters of the polymeric matrix composite detected and resolved by TSCr.

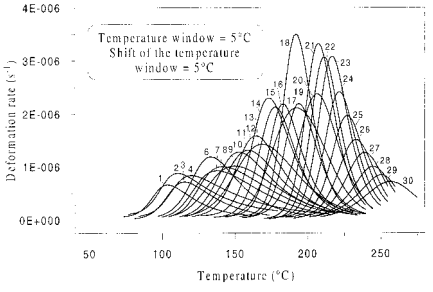


Figure 5 TSCr elementary spectra of KMU-4*l* composite in the region of α-relaxation measured with a shift of the stress temperature window of 5°C (strong aging).

Table I Parameters of Elementary Relaxation Processes in KMU-4*l* Composite Material Measured with a Shift of the Stress Temperature Window of 10°C (Weak Aging)

Process No., i	$T_{1\sigma_i}$ (°C)	T_{m_i} (°C)	ΔH_i (kJ/mol)	τ_{0i} (s)	Submode
1	90	93	—	—	—
2	100	117.0	109	$1.2 \cdot 10^{-12}$	—
3	110	120.0	151	$5.0 \cdot 10^{-18}$	$C_{\alpha\ \mathrm{low}}$
4	120	135.0	162	$1.4 \cdot 10^{-18}$	$C_{\alpha\ \mathrm{low}}$
5	130	143.5	150	$1.0 \cdot 10^{-16}$	$C_{\alpha\ \mathrm{low}}$
6	140	156.5	162	$1.2 \cdot 10^{-17}$	$C_{\alpha\ \mathrm{glass}}$
7	150	167.0	154	$9.5 \cdot 10^{-14}$	$C_{\alpha\ \mathrm{glass}}$
8	160	174.5	177	$2.5 \cdot 10^{-18}$	$C_{\alpha\ \mathrm{glass}}$
9	170	184.5	254	$1.7 \cdot 10^{-26}$	$C_{\alpha\ \mathrm{glass}}$
10	180	192.5	299	$5.4 \cdot 10^{-31}$	$C_{\alpha\ \mathrm{glass}}$
11	190	203.5	228	$1.0 \cdot 10^{-22}$	—
12	200	213.0	335	$3.2 \cdot 10^{-33}$	$C_{\alpha\ \mathrm{upper}}$
13	210	222.0	343	$1.7 \cdot 10^{-33}$	$C_{\alpha\ \mathrm{upper}}$
14	220	235.0	264	$1.3 \cdot 10^{-24}$	$C_{\alpha\ \mathrm{upper}}$
15	230	246.5	239	$1.9 \cdot 10^{-21}$	$C_{\alpha\ \mathrm{upper}}$

This consideration can explain the origin of the advantageous properties peculiar to KMU-4*l* composite such as outstanding strength resistance and stability of the thermal mechanical behavior within the interval of extreme operation temperatures typical for "Mir"-type space stations.

Upon aging inherent to repeated quench between 260 and 0°C, a broadening of the ΔH_i and τ_{oi} distributions is observed. The corresponding compensation lines are drawn in Figure 7. It is important to note that the cooperativity is getting higher when the number of quenches is greater than 12.

Cooperativity of Molecular Mobility

Three cooperative submodes can be distinguished on the compensation diagram (Fig. 7). The molecular mobility assigned to the glass transition has a compensation time τ_c = 1.7 s, and a compensation temperature T_c = 222°C (Table III), which is 17°C higher than the material T_g. The compensation time τ_c is low regarding the values of τ_c reported for polymers with flexible chains.[5,6] Such values of compensation parameters correspond to movement of nanometric sequences with strong interactive forces located in polymeric matrices with very compact microstructure.

It was found that the α-mode shifts by 27°C towards higher temperatures if the sample becomes strongly aged (Fig. 7). This phenomenon is interrelated with a rise in the fragility of the material that reduces its resistance to crack initiation and growth especially if the structure operates under external mechanical strains.[12] In comparison to the consequence of repeated TSCr quenches performed within the interval 260 to 0°C, the low-amplitude thermal cycling in real-space environments leads to the same kind of aging (ΔT_α = 30°C in Fig. 3). One can conclude that the TSCr method permits matching of a regime of simulated thermal aging to achieve the effect induced by prolonged low-amplitude thermal cycling upon the samples exposed to a space environment.

Comparison of TSCr and DMA Data

The characteristics of high-temperature relaxation processes in KMU-4*l* obtained by TSCr have been compared with DMA measurements represented in ref. 13. Three successive scans of DMA have been performed on the same sample. The tan $\delta(T)$ peak position (the α-relaxation temperature $T_{\alpha\ \mathrm{DMA}}$ corresponding to the first scan; another option is to consider dG'/dT minimums), T_g, T_c, and $T_{\alpha\ \mathrm{TSCr}}$ are as follows: $T_{\alpha\ \mathrm{DMA}} = T_g - 10°\mathrm{C} = T_c - 27°\mathrm{C} = T_{\alpha\ \mathrm{TSCr}} + 8°\mathrm{C}$. When the temperature $T_{\alpha\ \mathrm{TSCr}}$ is getting close to T_c due to increase in the number of quenches, we observe narrowing and intensifying of the TSCr complex spectrum (Fig. 6) despite the range of the activation en-

Table II Parameters of Elementary Relaxation Processes in KMU-4*l* Composite Material Measured with a Shift of the Stress Temperature Window of 5°C (Strong Aging)

Process No., i	$T_{1\sigma_i}$ (°C)	T_{m_i} (°C)	ΔH_i (kJ/mol)	τ_{0i} (s)	Submode
1	95	104.5	137	$7.1 \cdot 10^{-17}$	—
2	100	111.5	125	$6.6 \cdot 10^{-15}$	$C_{\alpha\ \mathrm{low}}$
3	105	116.5	137	$3.6 \cdot 10^{-16}$	$C_{\alpha\ \mathrm{low}}$
4	110	121.5	126	$1.5 \cdot 10^{-14}$	$C_{\alpha\ \mathrm{low}}$
5	115	—	—	—	—
6	120	134.0	141	$6.3 \cdot 10^{-16}$	—
7	125	138.5	128	$3.5 \cdot 10^{-14}$	—
8	130	141.5	151	$7.4 \cdot 10^{-17}$	—
9	135	149.0	121	$6.9 \cdot 10^{-13}$	$C_{\alpha\ \mathrm{glass}}$
10	140	150.5	176	$1.7 \cdot 10^{-19}$	$C_{\alpha\ \mathrm{glass}}$
11	145	159.5	148	$1.1 \cdot 10^{-15}$	$C_{\alpha\ \mathrm{glass}}$
12	150	166.0	165	$1.9 \cdot 10^{-17}$	$C_{\alpha\ \mathrm{glass}}$
13	155	171.5	105	$2.9 \cdot 10^{-10}$	$C_{\alpha\ \mathrm{glass}}$
14	160	174.5	203	$2.2 \cdot 10^{-21}$	$C_{\alpha\ \mathrm{glass}}$
15	165	179.5	214	$2.6 \cdot 10^{-22}$	$C_{\alpha\ \mathrm{glass}}$
16	170	184.5	258	$6.0 \cdot 10^{-27}$	$C_{\alpha\ \mathrm{glass}}$
17	175	193.0	199	$1.5 \cdot 10^{-20}$	$C_{\alpha\ \mathrm{glass}}$
18	180	193.0	285	$2.1 \cdot 10^{-29}$	$C_{\alpha\ \mathrm{glass}}$
19	185	196.0	267	$3.7 \cdot 10^{-27}$	$C_{\alpha\ \mathrm{glass}}$
20	190	198.0	231	$4.2 \cdot 10^{-23}$	$C_{\alpha\ \mathrm{glass}}$
21	195	208.0	320	$4.6 \cdot 10^{-32}$	$C_{\alpha\ \mathrm{glass}}$
22	200	212.0	347	$1.2 \cdot 10^{-34}$	$C_{\alpha\ \mathrm{glass}}$
23	205	206.0	349	$3.5 \cdot 10^{-35}$	$C_{\alpha\ \mathrm{glass}}$
24	210	211.0	380	$3.3 \cdot 10^{-38}$	$C_{\alpha\ \mathrm{glass}}$
25	215	217.5	371	$1.4 \cdot 10^{-36}$	—
26	220	224.5	410	$5.5 \cdot 10^{-40}$	$C_{\alpha\ \mathrm{upper}}$
27	225	233.0	368	$4.0 \cdot 10^{-35}$	$C_{\alpha\ \mathrm{upper}}$
28	230	243.0	282	$7.4 \cdot 10^{-26}$	$C_{\alpha\ \mathrm{upper}}$
29	235	255.0	208	$4.0 \cdot 10^{-18}$	$C_{\alpha\ \mathrm{upper}}$
30	240	267.0	—	—	—

thalpy ΔH_i and retardation time τ_i values becomes significantly broad, as shown in Figures 6 and 7.

The micromechanical parameters deduced from TSCr elementary spectra can be used to predict evolution of the high-temperature retar-

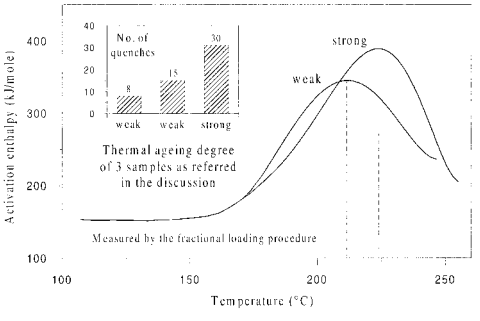


Figure 6 Evolution of the activation enthalpy as a function of thermal aging of samples of KMU-4*l* composite undergone repeated quenches in the range [260°, 0°C].

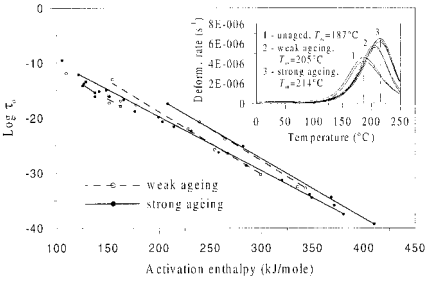


Figure 7 Compensation diagrams and TSCr complex spectra of two unequally aged KMU-4*l* samples due to a series of quenching (15 quenches—weak aging, 30 quenches—strong aging).

Table III Compensation Parameters of the High-Temperature Mode of KMU-4*l* Composite

Weak Aging			Strong Aging		
Submode	T_c (°C)	τ_c (s)	Submode	T_c (°C)	τ_c (s)
$C_{\alpha\ low}$	183	1.01	$C_{\alpha\ low}$	133	26.6
$C_{\alpha\ glass}$	222	1.7	$C_{\alpha\ glass}$	248	0.24
$C_{\alpha\ upper}$	156	$1.73 \cdot 10^7$	$C_{\alpha\ upper}$	193	$1.64 \cdot 10^5$

dation mode as a function of frequency. By making an assumption about monokinetic behavior of each i process, we can associate the equivalent frequency $f_{i\text{eq}}$ to each point $\tau_i(T_{m_i})$ on the picture of TSCr elementary spectra by the following relationship:

$$f_{i\text{eq}} = \frac{1}{2\pi\tau_i(T_{m_i})}, \tag{5}$$

where T_{m_i} is the temperature of the maximum of the i process. The absolute value of τ_i on Arrhenius diagrams of the measured samples of KMU-4*l* composite is about 2.65 s and almost insensitive to variation of T_{m_i} and to thermal aging of the material. Consequently, the equivalent frequency proper to the TSCr measurements is found to be $6 \cdot 10^{-2}$ Hz. The complex TSCr spectrum can be considered as a set of points with the frequency $f_{i\text{eq}}$, i.e., it corresponds in this case to an isofrequency at $6 \cdot 10^{-2}$ Hz. This will allow us to establish conformity between TSCr and DMA complex spectra.

To calculate the mechanical loss compliance J'' of KMU-4*l* as a function of temperature and frequency, the creep behavior of the composite material was considered after the Kelvin-Voigt model.[14] Then, the τ_{oi}, ΔH_i and ΔJ_i values extracted from the above-described TSCr analysis of elementary processes allow prediction of the loss compliance by the following relationship:

$$J''(\omega, T) = \sum_i \Delta J_i \frac{\omega\tau_i(T)}{1 + \omega^2\tau_i^2(T)}, \tag{6}$$

where ω is the angular frequency, ΔJ_i is the variation of the compliance proportional to the surface of the i process. The retardation time $\tau_i(T)$ is obtained by Arrhenius eq. (2). The summation is made over all elementary processes. In the theory of dynamic mechanical relaxation, the loss compliance $J''(\omega,T)$ represents the viscoelastic behavior of the material, and it can be deduced from spectra of the bending modulus $M'(\omega,T)$ and mechanical loss tangent tan $\delta(\omega,T)$:

$$J''(\omega, T) = \frac{M''(\omega, T)}{M'^2(\omega, T) + M''^2(\omega, T)}. \tag{7}$$

By using relationship (6), we have predicted the profile of the loss compliance J'' spectrum for KMU-4*l* composite as a function of temperature and frequency. Figure 8 shows the Arrhenius diagram corresponding to the reciprocal temperature $1/T_m$ of $J''(\omega,T)$ maximums in a range of frequencies 0.001 to 100 Hz. The points of $J''(\omega,T)$ peaks calculated from the DMA made at 2, 5, and 10 Hz (7) are also put on the Arrhenius diagram. It should be noted that the frequency-temperature dependence is an invariant regarding orientation and thermal history of the material. The superposition observed in Figure 8 shows that the TSCr and DMA mechanical spectra are coherent.

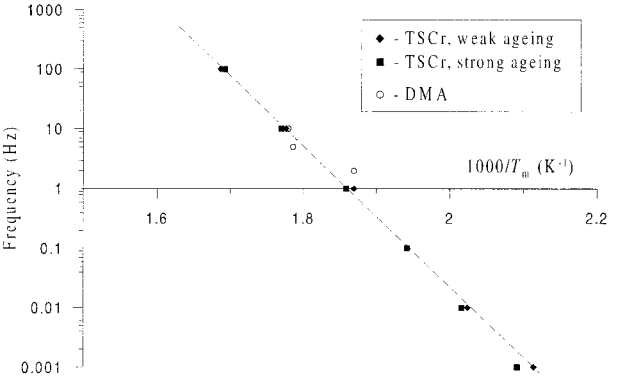


Figure 8 Arrhenius diagram for a series of frequencies as a function of reciprocal temperature for KMU-4*l* composite derived from the TSCr study compared to DMA data.

CONCLUSION

This study has shown the global thermomechanical response of KMU-4*l* composite used as a structural material on space stations and its evolution upon thermal aging. Complex TSCr spectra show a broad α-relaxation peak that is shifted by 27° towards higher temperatures upon thermal aging. The characteristic parameters of both the TSCr and DMA spectra are coherent.

The low value of the equivalent frequency inherent to the TSCr measurements ($6 \cdot 10^{-2}$ Hz) is the reason of high sensitivity of this method. Owing to this, the complex viscoelastic response has been experimentally resolved into a set of elementary processes that follow an Arrhenius law. Three cooperative submodes have been distinguished; the corresponding activation parameters obey a compensation law and strongly depend upon the thermal history of the composite due to postcuring phenomena. The broad activation enthalpy distribution indicates at a strong delocalization of molecular mobility. The evolution of those parameters may be a consequence of the increase of local order responsible for a deterioration of the impact strength of the composite material.

Thermal cycling in a low Earth orbit is the most important reason for physical aging of materials of spacecraft structures. Postcuring of epoxy matrices is its primary consequence; the secondary consequence is the formation of extra crosslinking in the postcured matrix. The same effect occurs when measuring properties of polymers by thermal experimental techniques. Therefore, the main concern is that the thermomechanical evolution affecting the parameters of TSCr spectra remains negligible regarding effects of solar UV radiation, charged particles, and thermal cycling of a real space environment. Thus, the main difficulty in laboratory estimation of physical properties of exposed specimens is usual weakness of these effects accompanied with some forms of degradation recovery. TSCr and DMA methods would allow differentiation of environmental effects and thermal aging induced by the experimental technique provided that the researcher always follows the same protocol and knows the exact thermal history of samples sensitive to postcuring degradation.

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