Multiphase Polymeric Composite Materials' CTE Variation with Extreme Environmental Conditions

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Coefficient of thermal expansion of multiphase composite materials plays an important role in the process of engineered materials design especially while approaching thermal management issues. Tailoring and designing material combinations in order to develop a composite structure to prove stability over a wide range of temperatures, from cryogenic to high values, to withstand extreme environmental conditions is the dream and purpose of any engineering team involved in such study/research area. The paper aims to approach and present the variations of the CTE with extreme environmental conditions (e.g. cryogenic conditioning) for particular combinations of particle-fibers multiphase polymeric composite materials. Influencing factors will be underlined to accompany the experimental research.

Keywords: multiphase, polymer, composite, cryogenic, coefficient of linear thermal expansion

The development of heterogeneous engineered materials, such are the multiphase polymeric composites, requires combined knowledge and skills, both theoretically and experimentally, in order to provide a material combination with desired thermo-mechanical and physical properties for structural components from a given application [1, 3]. Nonetheless, these new emerging materials have to withstand the same environmental conditions as their classical counterparts, even improved and more reliable to prove their consistency, development and manufacturing.

Multiphase polymeric composites have found a niche into engineering applications that involve extreme environmental conditions, such as cryogenic, high temperature or fluctuations between these, including humid conditioning, as materials for structural components in aero-space (e.g. rocket nozzles, fuel tanks,), civil engineering (e.g. liquid tanks), mechatronics (e.g. electronic packaging, sensors/actuators), electrical (e.g. electrical contacts, electrical shields), automotive (e.g. drive shafts, cylinders, brake rotors) or manufacturing (e.g. bearings, pistons) industries [4, 5, 8-10].

All the engineering applications of these multiphase polymeric composite materials require controlled thermal expansion characteristics in order to match those of other components and low values of the property to attain a good dimensional stability. With respect to the stability issue, this can be view from two perspectives: a change in the geometrical form – materials CTE (i.e. CTE - coefficient of thermal expansion) is playing a key role and a change in mechanical properties – a mismatch between the constitutive have a dominant effect.

In order to design a proper multiphase composite material for the previous mentioned engineering applications, to withstand extreme environmental condition, a lower CTE is desired. Following this objective, an attempt has been made to study and present the CTE behaviour for self-made multiphase polymeric composite materials combinations, with and without extreme environmental conditioning - such are the cryogenic temperatures - to identify, to size and to tailor the major influencing factors in order to address thermal management issues.

Experimental part
Materials and environmental conditioning

The multiphase composite samples were manufactured as having three phases – random fibers and particles - embedded in different volume fraction into a polymeric matrix. The matrix material is commercially known as SYNOLITE 8388 P2 from DSM COMPOSITE RESINS (Switzerland), a polyester resin type.

The particle inclusions considered were ceramic materials (with a high content of Al_2O_3), made from a natural stone, characterized as having a relatively high purity and provided by Alpha Calcite, Germany under the ALFRIMAL registered trade-mark and technical pure iron, respectively. Both particle types were mixed within the polyester resin mass in 5 and 10% volume fraction, respectively.

The 3rd phase chosen were E-glass type random fibers, commercially available under MultiStratTM Mat ES 33-0-25 trade name, from Johns Manville, SUA, mixed as having a 65% volume fraction in the overall composite volume. The reference sample was made without any particle content and used for comparison purpose.

The samples were conditioned within a temperature controlled oven to a cryogenic regime, 7 days long, 24 h/day, at a constant temperature of -35⁰C. The temperature intervals corresponding to the cooling down and room temperature recovering steps, at the beginning and at the end of the extreme environmental conditioning, approximately 2 h each, are inertial effects and were included within the overall cycle.

CTE testing procedure

The CTE measurements were performed using a DIL 420 PC differential dilatometer from NETZSCH GmbH (Germany). The composite samples were shaped into rectangular bars of about 5x5x25 mm³ and the transversal external surfaces were polished to guarantee plan-parallel surfaces for precise positioning within the measuring head. Each sample was subjected to two successive heating stages in order to size the influence of the thermal cycling on the samples' CTE variation. The temperature variation was set up having a linear trend from 20 to 250⁰C, at a heating rate of 1 K/min, into a static air atmosphere. To
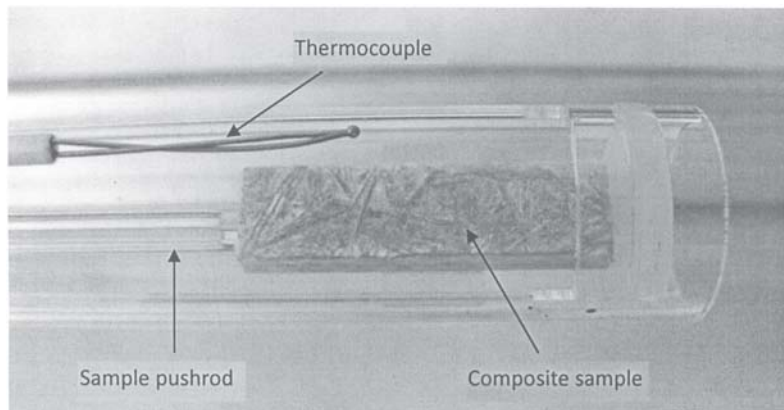
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Fig. 1. The measuring head – thermocouple and composite sample positioned inside the differential dilatometer DIL 420 PC
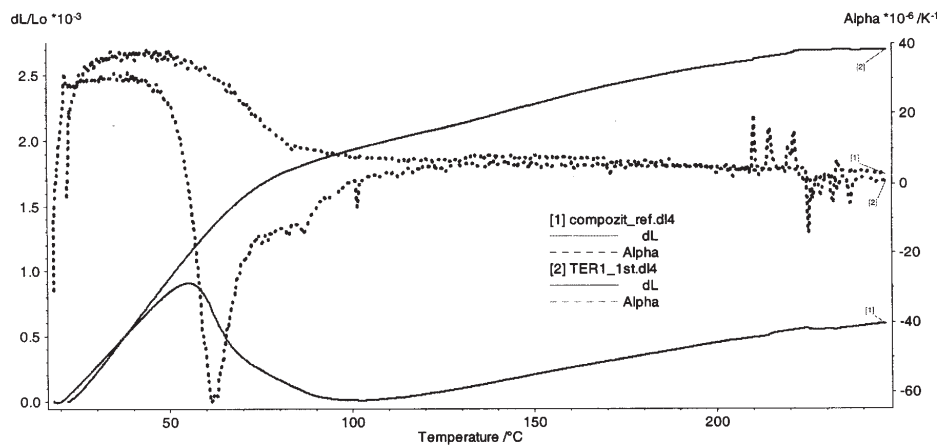

Fig. 2. Combined thermal strain and coefficient of thermal expansion vs. temperature range for the reference sample – first heating cycle, with and without conditioning at cryogenic temperature
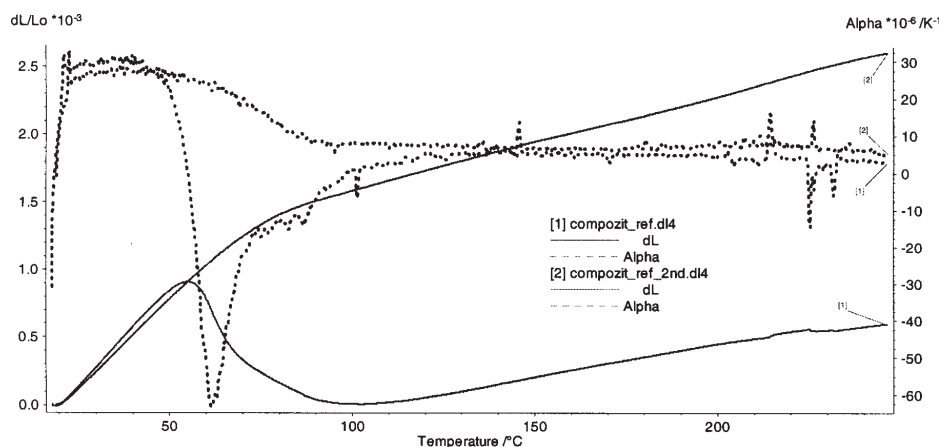

Fig. 3. Combined thermal strain and coefficient of thermal expansion vs. temperature range for the reference sample – 2 successive heating cycles, without environmental conditioning

eliminate the systems errors, the dilatometer was calibrated by measuring a standard SiO_2 specimen under identical conditions. Dedicated software called Proteus Analysis, developed by the same company, was used for data display and processing.

Results and discussion

Figure 1 is showing the measuring head with the thermocouple positioned near the composite sample. The composite samples are positioned horizontally on two quartz beds. The measured experimental data were sent to a PC via an USB cable, the acquisition software displaying information regarding the thermal strain variation with the imposed thermal range. As was mentioned previously, a linear regime was imposed, temperatures rising linearly from 20 up to 250°C. The latter value is higher than the polymer glass temperature implying a special attention to the matrix related influences, which will be discussed subsequently.

The experimental data were exported to Excel 2007, subjected to few constrains in order to eliminate the extreme values and simple statistics were used to compute the mean values. Table 1 lists the mean values of the instantaneous coefficient of linear expansion of the composite samples for temperature intervals covering the whole measuring range for all the composite samples, with and without thermal conditioning. As it can be seen, there are differences among the coefficients for each composite class individually due to the environmental conditioning, as well as among the multiphase composites based on different particle reinforcements type and volume fractions.

These differences can be sized also on the experimental curves corresponding to the instantaneous coefficient of linear expansion, in figure 2 to figure 6. Three different regions can be identified for all the composite samples, according to the curve shapes – region I up to 50°C, region II – from 50 to 100°C, and region III – from 100 to 250°C.

Usually, within the literature are reported the CTE values for a specific temperature. The idea of reporting a mean value over a temperature range lied on the fundamental principles of thermal dilatations – measuring coefficients of linear expansions has to provide a linear variation of the
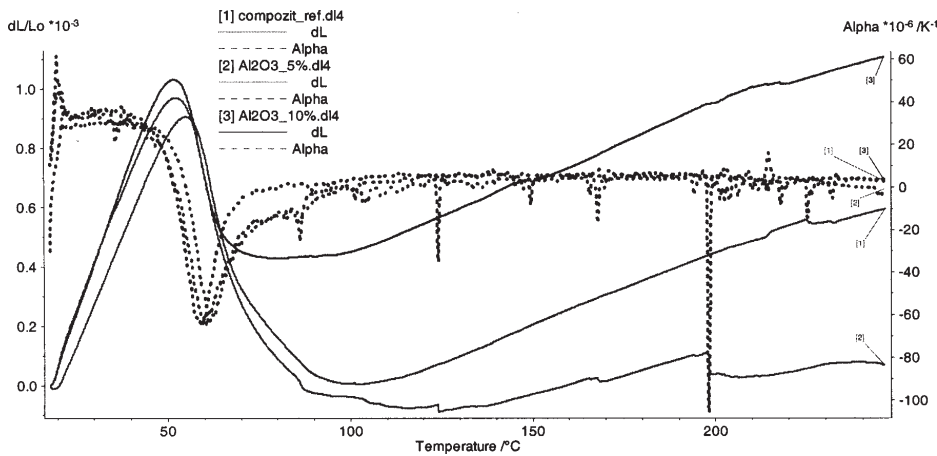
Fig. 4. Combined thermal strain and coefficient of thermal expansion vs. temperature range for the reference sample and both ceramic particle reinforced multiphase polymeric composite samples – first heating cycle, without environmental conditioning
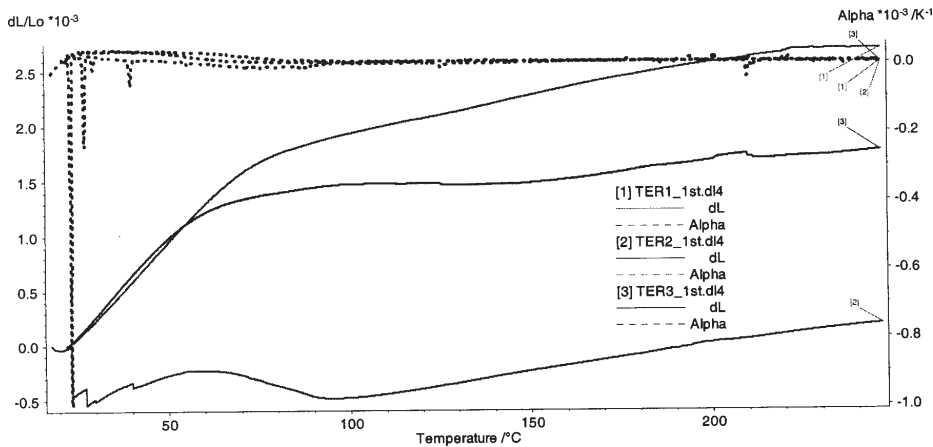

Fig. 5. Combined thermal strain and coefficient of thermal expansion vs. temperature range for the reference sample and both ceramic particle reinforced multiphase polymeric composite samples – first heating cycle, conditioned at cryogenic temperatures

property and any variations from this has to be regarded to the internal structure of the material under study or other influencing factors.

Figure 2 is showing both thermal strain and instantaneous coefficient of thermal expansion for the reference sample containing only the 5 layers of E-glass random fibers, with and without cryogenic conditioning. Within the region I the CTE values are almost linearly, in both cases, differences between the curves being relatively higher and revealing the environmental conditioning influence, whereas region II is revealing an abrupt decrease in the instantaneous CTE values based on the polymer chains reordering and chemical modifications as a part of an unfinished cure process. Region III is revealing a smother linear variation on both experimental curves, differences among the values being not as higher as in the first region. This variation can be regarded less to the polymer behaviour at temperature higher than its glass temperature but to the fibers reinforcements thermal behaviour.

The successive heating cycles do have an influence on both thermal strains and instantaneous coefficient of thermal expansion of the composite materials, as it can be seen from figure 3. The experimental data retrieved for

the reference sample reveal the polymer behaviour under temperature variations, the more cycling the most stable the overall composite, the resin polymerization reaching its final stage. A maximum value of the linear CTE was recorded at 22.1^0C with an onset at 45.4^0C for the first thermal cycling, whereas in case of the second cycling the peak was reached at 55.9^0C.

In table 2 are the temperature values recorded for each composite sample under discussion, with or without thermal conditioning at extreme environmental conditions, at which a maximum value of instantaneous linear CTE is being retrieved experimentally. These temperature values can be viewed as an overall behavior of the polymeric multiphase composite samples as experiencing a linear increase of a temperature in their surrounding environment and not necessarily as a compulsory measure for the composites performance.

The particle types, either ceramic (e.g. Al_2O_3) or metallic (e.g. Fe) and particle volume fraction do not have a major influence on the overall linear CTE of the multiphase composite material, with or without environmental conditioning, mainly due to the reduced volume fraction in which were embedded. This behaviour can be sized in the

Table 1

CTE VARIATION OVER THE TEMPERATURE RANGE FOR THE INVESTIGATED COMPOSITES

T [^0C]	Reference sample		5% Al$_2$O$_3$ (x10^{-6} /K)		10% Al$_2$O$_3$ (x10^{-6} /K)		5% Fe (x10^{-6} /K)		10% Fe (x10^{-6} /K)	
	without cond.	with cond.	without cond.	with cond.	without cond.	with cond.	without cond.	with cond.	without cond.	with cond.
20-50	23.06	34.93	31.36	24.14	33.38	36.93	31.90	33.15	32.30	36.37
50-100	21.80	15.87	26.07	26.77	27.76	35.86	25.04	30.04	29.62	34.40
100-150	4.105	6.159	4.557	4.564	5.094	4.935	4.443	4.748	4.640	4.936
150-200	4.074	6.043	3.936	4.312	4.148	4.306	4.847	4.994	4.730	5.211
200-250	4.261	4.132	3.111	3.481	3.508	2.914	4.941	4.969	4.698	3.983

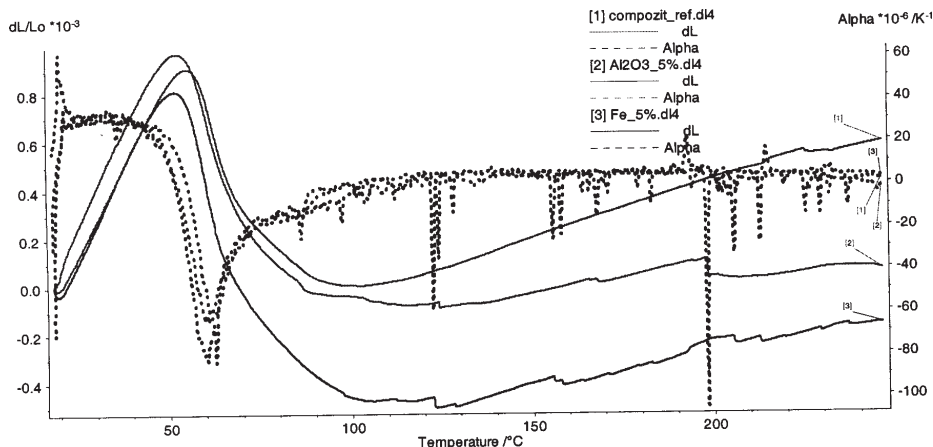|	Ref. sample	5% Al$_2$O$_3$	10%Al$_2$O$_3$	5% Fe	10% Fe	
no environ. conditioning	22.1^{0}C	124.4^{0}C	79.9^{0}C	123.4^{0}C	118.8^{0}C	**Table 2** TEMPERATURE VALUES AT WHICH MAXIMUM CTE ARE REACHED FOR EACH SAMPLE
thermal conditioning	53.5^0	95.3^{0}C	209.5^{0}C	103.9^{0}C	98.9^{0}C	

Fig. 6. Combined thermal strain and coefficient of thermal expansion vs. temperature range for the reference sample and the same particle volume fraction (e.g. 5%) but different materials multiphase polymeric composite samples – first heating cycle, without environmental conditioning

figure 4 to figure 6. In case of cryogenic conditioning the samples are showing a smooth variation over the temperature range of their instantaneous coefficient of linear expansion.

It is acknowledged from literature that increasing the particle volume fraction the overall linear CTE experience a slightly decrease [5, 7]. This behaviour is being used to address stability issues. Unfortunately, as it can be seen from the values provided in table 1, the instantaneous linear CTE slightly rise with the particle volume fraction content for the same temperature range. From authors' point of view this behaviour does not necessarily has to be regarded as a drawback but manufacturing related influencing factors has to be identified, such as non-uniform dispersion of the particles over the entire volume of the polymeric composite. In the same table, over the entire temperature range the overall CTE for each composite sample, individually, is experiencing a decrease.

Conclusions

The instantaneous coefficient of linear thermal expansion in case of multiphase polymeric composite materials is not an invariant value, being very sensitive to the heterogeneities and environmental conditioning of the measured samples. Its temperature dependence reflects phase changing, degree of polymerization, differences in internal structure, external environmental conditioning and the evolution of the internal thermal strain.

Thermal management issues can be addressed after thermal properties measurements on several multiphase composite structures based on a tailoring process for different combinations among the phases, theoretical predictions and an optimization approach.

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