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Review on Thermomechanical Anlysis of Nano Composites

Y.Sowjanya[1], V.Jayaprasad[2], K.Dileep Kumar[3], N.Mohanrao[4]
University College of Engineering Kakinada (Autonomous) Jawaharlal Nehru Technological University Kakinada

Abstract: *A Thermo-Mechanical Analysis (TMA) technique is used to investigate the compatibility & suitability of materials, physical & mechanical characteristics of materials and its optimum processing conditions. It measures the dimensional changes of a sample as a function of time, temperature and force in a controlled atmosphere. This TMA is used to access the glass transition temperatureT_g, melting point temperatures, coefficient of thermal expansion (CTE), deformations and viscoelastic measurements. It can be seen that polymers (ex: glass fibres) expand linearly at relatively low temperatures and gradually develops a varying expansion rate at high temperatures. Further increase of temperature eventually leads to an abrupt change in length at glass transition region (T_g). In this paper investigation on thermal behaviors of glass fibers, polypropylene/ calcium carbonate nano composite and Nanosilica Reinforced PEEK Composites are presented.*

Keywords: *Thermo Mechanical Analysis, Probes, Nano Composites, Coefficient of thermal expansion, Glass transition temperature.*

I. Introduction

The study of relationship between a sample property and its temperature as the sample is heated or cooled in a controlled manner is referred to as Thermal Analysis (TA). The main TA techniques used for thermal characterization of the matrix resin compositions, composites and their raw materials are Differential Thermal Analysis(DTA), Differential Scanning Calorimetry (DSC), Thermo Gravimetric Analysis (TGV), Thermo Mechanical Analysis (TMA) and Dynamic Mechanical Thermal Analysis (DMTA). Among this TMA is the most important characterization technique in the field of Thermal Analysis (TA). With TMA, sample dimensional properties are measured as the sample is heated, cooled or held under various boundary conditions. The force applied to the sample can be varied with TMA. This technique is used to access the properties of polymers like softening temperature (T_g), melting temperature, stress relief effects at T_g, coefficient of thermal expansion(CTE), dimensional capabilities of two or more different materials, composite de lamination temperatures, shrinkage forces, testing of coatings on metals, films, optical fibers and electrical wires .The measurements can be carried out by the number of different probe configurations. Depending on the applied load experiments may be done in compression, tension, shear, torsion, penetration or some bending mode etc.

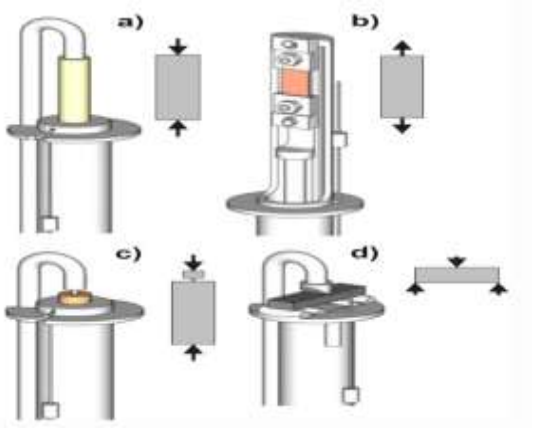


Figure1: Deformation modes in TMA a)Compression b)Tension c)penetration d) 3-point bending

The choice of measurement of mode depends on the studied properties, shape of the sample and its applications. The most useful modes of measurements are compression (for self supporting samples) and expansion (for thin films and fibres).These modes are mainly used to determine glass transition temperatureT_g, thermal expansion coefficients. The sample is placed in an enclosure and is in contact with a probe leading to a displacement sensor. A small force is applied to keep the probe in contact with the sample. This equipment operates over a temperature range of -150^oc to 1000^oc using heating rates up to 10^oc/min and expansion of

the sample was measured by displacement sensor. In this paper, we aimed to study the previous literatures regarding the thermal behaviors of boron free E-glass fibres, polypropylene calcium carbonate nano composites, nanosilica reinforced PEEK composites by developing a protocol in a commercial TMA. The established procedure allowed us to characterize the coefficient of linear thermal expansion and T_g of glass fibre over a broad temperature range from -150^{o}c to 1000^{o}c. The effect of thermal compaction was also investigated by the characterization of isothermal change in material length and longitudinal modulus after heat treatment. Furthermore the measured property values are compared before and after heat treatment. The phenomena of thermal expansion can challenging when designing buildings, bridges, aircrafts and space crafts, but it can put beneficial uses like thermostats and other heat sensitive sensors etc.

Coefficient of Linear Thermal Expansion is a fundamental thermo mechanical characteristic of a material and it is determined by the composition and structure of the material. CLTE describes the relative change in length of material per degree temperature change. The L_1 and L_2 are specimen lengths at temperatures T_1 and T_2.L_0 is the length at a reference temperature, then the coefficient of linear thermal expansion can be written as

$$\propto = (L_2\text{-}L_1) / \{L_0(T_2\text{-}T_1)\} = \Delta L/L_0\Delta T$$

The CLTE is used to measure changes in length, width and thickness of a modulated part with changes in temperature. Addition of fillers, such as glass, significantly alters the CLTE of a polymer. Polymers may be formulated with CLTEs to match those of metal or other materials used in complex components, such as automotive parts.

II. Experimental Analysis

2.1. Specimens And Its Operating Conditions

2.1.1. Boron Free E-Glass Fiber:

A boron free E-Glass fibre supplied by Owens Croning vertrotex was investigated in this work. The roving's had a nominal tex of 1200 and single fibre diameter of 17.4 $\pm$1.3 µm. Before coated with a normal rotating cylinder sizing applicator containing a 1% γ aminopropylsilane (APS) hydrolyzed in distilled water, the molten fibres had been hyper quenched with water supply. To investigate the effect of temperature on structural changes in glass fibre, samples were kept at a range of elevated temperatures and isothermal changes were measured as a function of time. In addition young's modulus of glass fibre was measured either at different temperatures from 20^{o}c to 700^{o}c with a increment of 20^{o}c or at a room temperature after heat treatment for 30 minutes from 50^{o}c to 650^{o}c with a increment of 50^{o}c. The modulus was obtained from stress-strain curves generated by force ramp rate of 5mN/min until 20Mn is reached.

2.1.2. Polypropylene calcium carbonate nano composite:

Polymer nano composites (PNC s) are formed from blends of nano meter sized fillers with either thermo plastic or thermo setting polymers. PNCs improve mechanical properties, barrier properties heat resistance, dimensional stability and flame retardency. Here PNC s are formed by mixing polypropylene with calcium carbonate nano composites. The dimensions of polypropylene $CaC0_3$ nano composite test sample for testing thermal behavior using TMA are 5 mm× 5mm ×3.2674 mm (Length × Width × Thickness),and the scanning range is from 40^{o}c to 152.24^{o}c at a heating rate of 5^{o}c/min and at fixed load of 0.02 N under nitrogen atmosphere.

2.1.3. Nanosilica Reinforced PEEK composites:

Poly ether ether ketone (PEEK-50µm) nano composites with 30 nm silica incorporation were successfully fabricated through hot-press method. The dimensions of the nanosilica reinforced PEEK composite sample specimen for testing thermal behavior using TMA are 120mm×120mm×2mm (length × width × thickness), and the scanning range was from 30 to 250^{o}c at a heating rate of 2^{o}c/min and at fixed load of 0.05N under nitrogen atmosphere.

2.2. Selection of Modes of Deformation

The expansion, macro-expansion and penetration probes are supplied with Q400. These probes plus the flexure probe and the friction bending fixture are included with the Q400EM module. Data analysis programs relevant to each measurements described are provided in our $Advantage^{TM}$ software.

Figure2: Modes of deformation

2.2.1. Expansion probes:
It determines materials coefficient thermal expansion (CTE), Glass transition temperature, compression modulus. A flat-tipped standard expansion probe is placed on the sample and is subjected to temperature regime. Probe movement records sample expansion or contraction. This mode is used with most solid samples and the macro expansion probe is more effective for soft or irregular samples, powders, frozen liquids and films.

2.2.2. Penetration probes:
Penetration measurements use an extended tip probe to focus the drive force on a small area of the sample surface. This provides precise measurement of glass transition temperature, softening and melting behavior. It is valuable for characterizing coatings without their removal from a substrate. The probe operates like the expansion probe but under large applied stress. A hemispherical probe is an alternative penetration probe for softening point measurements in solids.

2.3. TMA procedure for test the samples

Thermo mechanical analyser Q 400 manufactured by TA instruments was used to measure change in length of sample as a function of temperature and time. The key components include a furnace system for providing a well controlled environment, stage/probe assembly for holding the specimen and movable core linear variable differential transducer whose output is proportional to displacement of the core caused by changes in the specimen dimension. Other important components involve a temperature sensor that can be placed in close proximity to the specimen and an electro chemical coil that can apply thermal force to the sample.

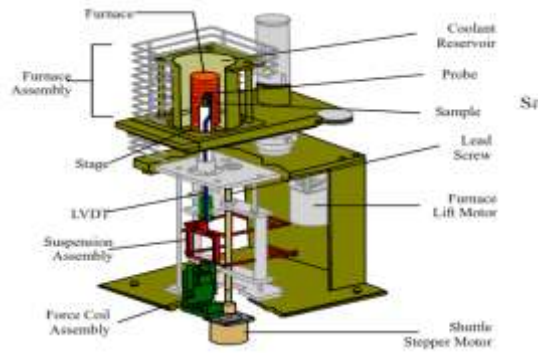


Figure 3: Schematic diagram of TMA Q400

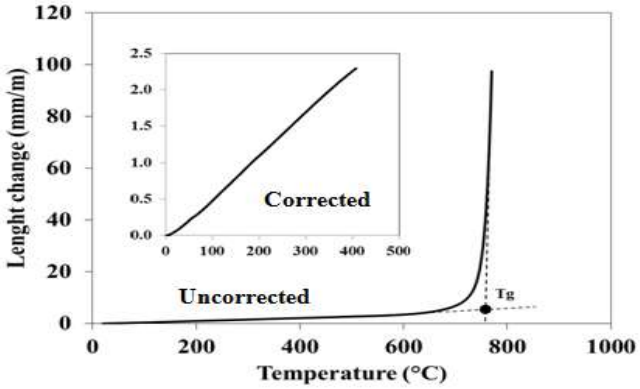
The samples of above mentioned dimensions were clamped in fixture on the thermo mechanical analyser. Before testing the sample, temperature on the analyser is set at room temperature 40^oc. Rate of heating o_C/min is 10^oc. select the probe as either expansion or penetration probes and the selected probe is set on the mind of the sample which is geometric centre of the square piece. A constant load is applied on the probe. Gradually increase the temperatures at heating rate of 10^oc/min, the change in the dimension to corresponding temperature observed and recorded. The analyser while the experiment is connected to a computer which is programmed to capture the reading through analysis software which plots the graph and it calculates the mean value of coefficient of thermal expansion using the displacement Vs temperature data obtained from software.

III. Results

3.1. Boron Free E-Glass Fiber:
Table1 summarize the results of CLTE and T_g obtained for a number of individual glass fibres up to 300^oC temperature at the heating rate of 5^oC/min.

Initial Sample length (mm)	CLTE within 20°C-300°C (µm/(m•°C))	Corrected CLTE (µm/(m•°C))	Tg (°C/min)
23.01	5.3	5.6	759
19.74	5.4	5.7	749
23.25	5.6	5.9	761
22.28	5.8	6.1	762
22.64	5.8	6.2	759
19.39	6.1	6.4	762
21.91	6.2	6.5	763

Table1: TMA results of single boron-free E-glass fibre at heating rate of 5°C/min

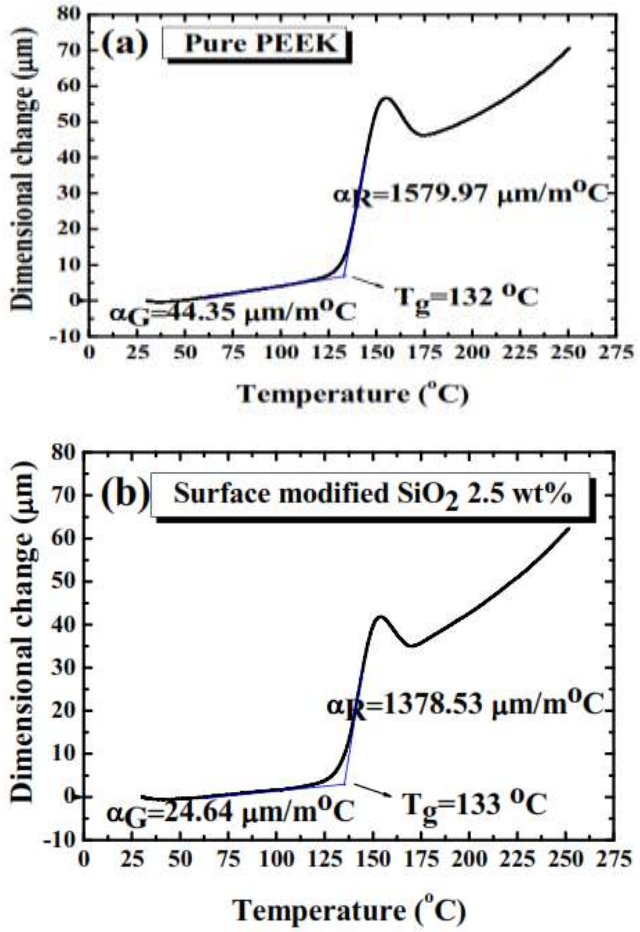


Graph 1: TMA plot for length change of a single glass fibre as a function of temperature

Above graph shows that the glass fibre expands linearly at relatively low temperatures and gradually develops a relatively low expansion rate at high temperature eventually leads to an abrupt change in the fibre length at glass transition region. T_g can be obtained by point of intersection of the tangents to length versus temperature before and after glass transition region.

3.2. Nanosilica Reinforced PEEK Composites:

The effect of nanofiller incorporation on the dimensional stability (CTE) and T_g of the resulting PEEK composites, as a function of nanosilica volume fraction, is established and the results are shown in bellow figure and table. In that both the composites with surface modified and unmodified are examined and compared.



Graph 2: TMA thermal scans on (a) Pure PEEK (b) 30nm silica filled PEEK nanocomposite with a filler content of 2.5 wt%. The glassy volume expansion coefficient (α_G), Rubbery volume expansion coefficient (α_R) and T_g values are shown.

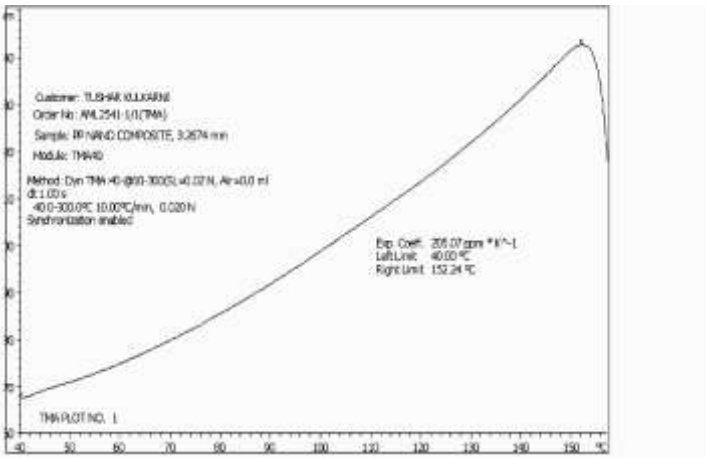
Table2 illustrates as the filler content increases,α_R of the nano-silica would decrease, irrespective of the modified or unmodified cases. It is known that the specific heat of silica is higher than that of PEEK polymer. The component of nano-sized silica could significantly increase the overall specific heat of the PEEK composite. The nano silica particles processing large specific areas would greatly absorb the heat transferred from the PEEK matrix and in turn greatly suppress the thermal expansion of the plastic PEEK polymer when the temperature is higher than T_g .The other reason for the reduction of α_R might be due to hindrance of the silica nano particles toward the expansion of PEEK chain segments themselves when the temperature is over T_g.The decrease in α_G of composites with lower amount of silica is also a result of the lower CTE value of the ceramic characteristics of silica, but when the nano-silica volume fraction is higher and the particle clustering becomes more severe, this effect becomes less and less evident.

Sample	**U or M**	**CTE**		T_g (o_C)
		α_G (µm/$m^o c$)	α_R (µm/$m^o c$)	
Pure PEEK		44.35	1576.0	132
Si$O_2$2.5 wt%	U	24.41	1207.2	132
	M	24.64	1378.5	133
SiO_2 5 wt%	U	31.27	1042.9	132
	M	40.88	1193.6	133
Si$O_2$7.5 wt%	U	43.45	585.3	133
	M	46.37	677.8	132
Si$O_2$10 wt%	U	41.88	210.2	134
	M	44.94	309.3	133

Table2. α_G and α_R for the 30nm unmodified-silica(U), modified-silica(M) filled PEEK composites are

3.3. Polypropylene/Calcium Carbonate:

Test Description	**Temperature range**	**Observed value**
CLTE in thickness direction	40-152.24	205.07×10-6 µm/$meter^o$C



Graph 3: TMA penetration curve on a PNC sample

The thermal curve generated from the actual experimentation values with ordinate taken as displacements ranging from 60-145µm and temperature on abscissa. It shows behavior of the nano composites while it is under the influence of gradual heat temperature range from 40 to 150^oc. The penetration probe starts deflecting as the temperature rises to 40^oc from 60-145 µm. The observation shows the nano composite maintains uniform curve throughout the temperature conditions. CLTE in thickness direction is 205.07 parts per million (micro meter per meter)/^{o}c

1. Future Scope

Polymer composites are engineering materials. Development of nano composites are used to fulfill the need of best material for the application in Defense, Automobiles, electronics, machines pertaining to low cost, light weight material.The coefficient of thermal expansion is one of the properties which have been focused to analyze a nano composite for the development better and efficient material for engineering applications. TMA equipment facilitates accurate and precise values for the variation of length due to effect of temperature. Therefore ensuring the capability, function ability, durability and safety of the part. The TMA analysis is made at micro level, the readings and observations are obtained very accurately.

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