Relationship between electrical and mechanical loss tangents of SLG reinforced phenolic composites: pilot study

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Abstract: The mechanical properties of ceramic microspheres (SLG) reinforced phenolic resin composites have been measured and evaluated in earlier studies. This basic but critical and important data have caused interests in the relevant industry in Australia. This study is therefore carried out to measure and evaluate the dielectric and mechanical properties of the composites with a view to benefit the relevant industry. The relationship between the two properties will also be studied. The original contributions of this paper are that samples post-cured in conventional ovens have higher electrical loss as well as mechanical loss than their counterparts post-cured in microwaves. The storage modulus of all samples post-cured conventionally is higher than its counterpart. This is in line with the fact that it is a softer material with lower glass transition temperature. They also have higher mechanical loss tangent as well as loss modulus. For all percentages by weight of SLG, the glass transition temperature for the microwave cured sample was higher and the composite was stiffer; the opposite was true for the conventionally cured sample.

Keywords: Phenolic resin, ceramic microspheres, dielectric loss tangent, mechanical loss tangent, glass transition temperature, storage modulus and microwaves

Introduction

The Centre for Excellence in Engineered Fibre Composites (CEEFC) at the USQ seeks to facilitate the development and introduction of lightweight composite materials into engineering commercial applications. Phenolic resins present excellent dimensional stability, thermal stability, chemical resistance, and load-bearing capability at elevated temperatures. However, the characteristic high crosslink density of the phenolic resins results in low impact resistance and brittleness [1]. In order to improve these mechanical properties, ceramic microsphere (SLG) was added to the resin and the fracture toughness, flexural strength and

tensile strength of the composites with varying percentage by weight of SLG had been evaluated [2-5]. In this study, the dielectric and thermal properties of the prepared composites were investigated. The percentage by weight of SLG was also varied to investigate what was the best percentage by weight of SLG as far as the two groups of properties studied.

The materials

The commercial resole resin used in this study was J2027and manufactured by Borden Chemical Pty. Its official name is now Hexion Cellobond J2027L because the company had been taken by Hexion [6]. The catalyst used to crosslink the resin is phenolic resin hardener catalyst produced by the same company. The official name of the catalyst is Hexion Phencat 15 [7]. The ratio by weight of the resin to hardener is 50: 1, which may be changed when the resin is supplied by other manufacturer.

Without filers or reinforcements, the parts are brittle and have high shrinkage in the mould because of the crosslinked nature of the cured resin. The most common filler is wood flour. Other common fillers and reinforcements are cotton fibres, fiberglass, chopped thermoplastic fibres, e.g. nylon.

The high number of OH groups in the resin gives it excellent adhesive qualities. However, this adhesive nature of phenolics causes moulding problems. They tend to stick to the moulds. Release agents have to be sprayed into the mould surface to solve this problem. The nonflammability of the resin leads to its wide applications. When phenol formaldehyde resin is subjected to a flame, they char rather than melt or burn. They are therefore widely applied

in situations where avoiding flammability and smoke is vital. Furthermore, the char has a very low thermal conductivity so that surrounding materials are protected by the decomposed phenolic. Low thermal conductivity of the resin promote its used as bases for toasters and knobs for appliances. Most phenol formaldehyde parts are dark because the dark colour is inherent to it and this also limits its use in some applications. A dark pigment is usually added to the resin to standardize the colour and to decrease its sensitivity to UV light. Its high electrical resistance wins its applications in electrical switches and circuit breakers. The abrasive nature of the phenolic formaldehyde makes its machining difficult; they are therefore moulded to near net shape. The resin is cured by condensation polymerization which results in the evolution of water as a by-product of the curing process and extensive microvoiding within the matrix. The microvoids have little effect on the composite properties except that significantly higher water absorption is observed. High water content can cause structures to delaminate when exposed to heat [8-9].

The Enviroshperes (E-spheres) SLG, is a mineral additive that can improve product by reducing product's weight, improving its performance and lowering its cost. E-spheres are white microscopic hollow ceramic spheres that are ideal for a wide range of uses. The particle size of this general purpose E-spheres ranges from $20 - 300$ μm with approximate mean of 130 μm. The relative density of E-spheres is 0.7. E-spheres are a combination of Silica, SiO_2 (55-60%), Alumina, Al_2O_3 (36-44%), Iron Oxide, Fe_2O_3 (0.4-0.5%) and Titanium Dioxide, TiO_2 (1.4-1.6%). E-sphere is an inert material similar to talc, etc. The material may be prone to dusting in use. Grinding, milling or otherwise generating dust may create a respiratory hazard. In high dust areas the use of goggles and a National Institute of Occupational Health and Safety (NIOSH) approved dust respirator is recommended.

They are used in a variety of manufacturing applications because of their unique properties and they are [10]:

- extreme heat resistance;

- high compressive strength;

- pure, clean and white.

In addition to these unique features, E-spheres provide all the benefits you would expect from a microsphere. The typical applications in composites include casting, spray-up, hand lay-up, cold/hot press molding, resin transfer molding and syntactic foam.

Sample post-curing

For the oven post-cured samples, after initial 24-hour curing at ambient conditions, the test pieces were removed from the mould, they were then post-cured. This was achieved by baking the pieces in an oven. Oven temperatures and times were:

- 4 hours at 50°C
- 4 hours at 80°C
- 2 hours at 100°C

For the microwave post-cured samples, after initial 24-hour curing at ambient conditions, the test pieces were removed from the mould, they were then post-cured in modified Sanyo microwave cavity; the microwave oven has a total power of 800 W; the power input could be varied in ten steps of 80 W. The power level used was 160 W as the 80 W was found to be too weak for this purpose; higher power levels were not recommended because it would cause the samples to cure swiftly, resulting in the formation of blowholes. The microwaves heated up the six specimens to 100 ^{o}C in 40 minutes and the temperature of the specimens was measured using an infrared thermometer. One hundred ^{o}C was chosen because when samples were cured in a conventional oven, the highest temperature reached was 100 ^{o}C.

They were then cooled to room temperature in the modified microwave oven cavity and then subjected to short bar tests [11].

Dielectric tangent loss

Dielectric properties can be used to classify materials as conductors, quasi conductors or insulators. The alternating polarisation of the molecules can consume energy, this is polarisation loss. A complex permittivity is required to characterise these materials. Materials can be good conductors at some frequencies while becoming a dielectric at other frequencies. A dielectric material is a substance that is a poor conductor of electricity, but an efficient supporter of electro static fields. An important property of a dielectric is its ability to support an electrostatic field while dissipating minimal energy in the form of heat. The lower the dielectric loss, the proportion of energy lost as heat, the more effective is a dielectric material. Samples of SLG reinforced composites cured conventionally and in microwaves were used to measure dielectric tangent loss of the material.

The complex relative permittivity of a dielectric is $\varepsilon = \varepsilon' - j\varepsilon''$; the real part is the dielectric constant; the imaginary part is referred to as the loss factor. The ratio of these two values is the loss tangent, $\tan \delta = \dfrac{\varepsilon'}{\varepsilon''}'$ [12]. The method used to obtain the dielectric tangent loss will be by measuring the capacitance and conductance with a meter.

Two copper plates will be used to form the parallel plate capacitor with a flat sample sandwiched between as the dielectric. The sample size should be at least 120 mm x 120 mm to ensure that it is an efficient supporter of electro static fields. The sample was cast into shape into a Teflon mould. One should be aware of air gap and hence the plate should not be

too large either. The set-up was then connected to LRC meter to complete the circuit for measurements. Probes are used to measure the capacitance and tangent loss. The values are read off the display and recorded onto a spread sheet for analysts. The loss tangents of oven-cured and microwave-cured samples with SLG percentages by weight vary from 0 to 15 % in step of 5 % were measured.

Figure 1 shows the schematic parallel connection of C and G. The distributed shunt capacitor, C and the conductance, G are both dependent on the properties of the dielectric material which separates the line conductors. The currents flowing through the parallel combination of C and G are shown in Figure 3(a) and their phasor relationship in Figure 3(b). From the measurements, the real and imaginary parts of the dielectric loss can be calculated from the following relationships [13]:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{s} \tag{1}$$

where C is the capacitance in Fm^{-1};

ε_0 is the dielectric permittivity of free space $= \dfrac{1}{36\pi} \times 10^{-9}$;

ε_r is the dielectric constant of the composite;

A is the surface area of the samples in mm^2;

s is the thickness of the composite sample in mm^2.

and
$$G = \frac{\sigma A}{s} \tag{2}$$

where G is the conductance of the composite in Sm^{-1};

A and s are the same as above.

and $$\sigma = \omega \varepsilon_0 \varepsilon'' \qquad (3)$$

where is the frequency in the range of 10 to 100 kHz [14].

and the loss tangent [12]

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

(4)

Loss tangent is frequency dependant. This experiment will be made at one hundred, 100, 120, 1k, 10k, 20k 100k. This is within the range of the measuring device.

If the properties of the dielectric are constant over the frequency range of interest, then C will be constant and G will be proportional to frequency, and the loss tangent can be easily calculated by the formula [14]:

$$G = \omega C \tan \delta \qquad (5)$$

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA is a technique used to study and characterize materials. It is most useful for observing the visco-elastic nature of polymers. Two methods are currently used. One is the decay of free oscillations and the other is forced oscillation. Free oscillation techniques involve applying a force to a sample and allowing it to oscillate after the force is removed. In this project, forced oscillation was employed. Forced oscillations involve the continued application of a force to the sample. An oscillating force is applied to a sample of material and the resulting displacement of the sample is measured. This method is the most commonly used one today. Samples can be either solids or melts. Most solids are tested by linearly

applying strains, and melts or liquids are normally tested in shear. The sample deforms under the load. From this, the stiffness of the sample can be determined, and the sample modulus can be calculated. By measuring the time lag in the displacement compared to the applied force it is possible to determine the damping properties of the material. The time lag is reported as a phase lag, which is an angle. The damping is called tan δ, as it is reported as the tangent of the phase lag. Visco-elastic materials such as polymers typically exist in two distinct states. They exhibit the properties of a glass (high modulus) at low temperatures and those of a rubber (low modulus) at higher temperatures. By scanning the temperature during a DMA experiment change of state, the glass transition or alpha relaxation, can be observed. The glass transition temperature (T_g) is often measured by DSC (Differential Scanning Calorimetry), but the DMA technique is more sensitive and yields more easily interpreted data. DMA can also be used to investigate the frequency (and therefore time) dependent nature of the transition. This is useful as the degree of dependence is specific to the transition type. T_g has a strong dependence on frequency but melting is frequency independent; DMA can also resolve sub-T_g transitions, like beta, gamma, and delta transitions as the DSC technique is not sensitive enough to pick them up in many materials that. In addition, DMA gives modulus values. Frequency is constant and the temperature is varied. Figure 4 is a schematic of a DMA system showing the heating element and movement coil [15].

In the test, an oscillating force is applied to a sample while the temperature is varied the resulting displacement of the sample is measured. The sample dimension used in the test was 60 mm x 10 mm x 4 mm; the frequency of oscillation was 1 Hz. UNIVERSAL ANALYSIS 2000, the software used, carries out the calculations. From these experiments, graphs of tangent delta loss and storage modulus were produced.

Results and discussion

Figures 2 through 5 are the loss tangents of PF/E-SPHERES with varying percentage of SLG by weight post-cured in oven and microwaves respectively. For the composites, it is necessary to divide the results into two groups: low frequency group (up to 1 kHz) and high frequency group (10 kHz and up). In low frequency group, for all SLG by weight, the microwave post-cured specimens have higher loss tangent values than their counterparts. The opposite is true for the higher frequency group. It can be argued that the dielectric behaviour of for the low frequency group is due to the fact that the change in polarity used in the study is too slow to initiate the change of polarity for water molecules; this results in low loss tangent values for materials supposed to have high water content. On the other hand, the dielectric behaviour of the other group (higher frequency) matches the neat resin specimens. The higher frequency group is more important because for most microwave processing of materials, the frequency used will be high, e.g. 2.45 GHz. In general oven cured samples have higher loss tangent values. This means that the curing by oven is not complete and it will be better to post-cure the composites by microwaves. On top of it, the time to post-cure the samples by microwaves is only 5 % of its counterpart [16].

The values of electrical loss tangent to that of the mechanical ones were now compared. For all samples, irrespective the percentage by weight of SLG, oven cured samples have higher modulus values, which imply that oven cured samples are softer material and this is at par with the glass transition temperature. In general oven cured samples have higher loss tangent as well as loss modulus. The higher loss tangent values are due to presence of water and lower degree of curing. Higher loss modulus means softer material, which in itself may

have higher water content and less degree of cure. Therefore, samples with low loss modulus also have low loss tangent because there will be moisture with lower degree of cure.

Figure 6 (for neat resin) shows that the glass transition temperatures for conventionally cured and microwave cured were 159.87 ^{o}C and 184.70 ^{o}C respectively. It also illustrates that the storage moduli of them are 2,142 MPa and 1,188 MPa respectively. The glass transition temperature for the microwave cured sample was higher and it was stiffer; its storage modulus was supposed to be higher as well but this was not the case. The situation is just the opposite for the conventionally cured sample. This does not match the phenomenon for most materials. However, the loss moduli of the microwave cured samples were lower than their counterparts for the range of temperature measured and this is correct because lower loss moduli mean stiffer material.

Figure 7 (for 5 % w/t of SLG) shows that the glass transition temperatures for conventionally cured and microwave cured were 154.53 ^{o}C and 201.77 ^{o}C respectively. It also illustrates that the storage moduli of them are 1,852 MPa and 1,838 MPa respectively. The glass transition temperature for the microwave cured sample was higher and the material was stiffer; its storage modulus was supposed to be higher as well but was not the case. The situation is just the opposite for the conventionally cured sample. This does not match the phenomenon for most materials. However, the loss moduli of the microwave cured samples were lower for the range of temperature measured than their counterparts and this is correct because lower loss moduli mean stiffer material.

For 10% SLG reinforced phenolic resins, the glass transition temperatures for conventionally cured and microwave cured were 192.13 ^{o}C and 149.65 ^{o}C respectively. It was also found

that the storage moduli of them are 1,234 MPa and 1,347 MPa respectively. The glass transition temperature for the microwave cured sample was lower and the material was softer; its storage modulus was supposed to be lower as well but was not the case. However, the loss moduli of the microwave cured samples were lower for the range of temperature measured than their counterparts and this is correct because lower loss moduli mean stiffer material.

For 15% SLG reinforced phenolic resins, the glass transition temperatures for conventionally cured and microwave cured were 189.08 ^{o}C and 152.86 ^{o}C respectively. It was also found that the storage moduli of them are 1,152 MPa and 1,630 MPa respectively. The glass transition temperature for the microwave cured sample was lower and it was softer; its storage modulus was supposed to be lower as well but was not the case. However, the loss moduli of the microwave cured samples were higher than their counterparts for the range of temperature measured and this is incorrect because higher loss moduli mean softer material.

By and large, for all percentages by weight of SLG, the glass transition temperatures for the microwave cured sample were lower and the material was softer; its storage modulus was supposed to be lower as well but was not the case. It is really very difficult to explain this phenomenon. On the other hand, for all percentages of SLG by weight except the 15 % one, the loss moduli of the microwave cured samples were higher than their counterparts for the range of temperature measured and this is incorrect because higher loss moduli mean softer material. The mechanical behaviour of the 15% SLG by weight is also difficult to explain. More study will be required to confirm these two strange phenomena.

In a previous study, the composites were post-cured in an oven, the Young's modulus of the neat resin was 2.51 GPa and it decreased slowly as the percentage by weight of SLG increased (up to 15 %) and dropped significantly to 1.39 when the percentage by weight of SLG was 20 %; after that the values did not change much [17]. The values found seem to be reasonable when they are compared with those of phenolic formaldehyde (2.76 – 4.83 GPa) [18].

In the same study, when the composites were cured in microwaves, the Young's moduli of varying weight E-sphere reinforced phenol formaldehyde matrix composite were also evaluated. The Young's modulus of the neat resin was 2.90 GPa and it dropped significantly to 1.70 GPa as the percentage by weight of SLG increases (up to 15 %) and dropped slowly to 1.57 when the percentage by weight of SLG was 25 %; after that the values rebounded but did not change much [19]. The values found seem to be reasonable when they are compared with those of phenolic formaldehyde (2.76 – 4.83 GPa) [20]. Moreover, the Young's modulus of pure phenolic resin in this study is 2.90 GPa, which is exactly the same found by Wang et al. for pure phenolic resin (2.9 GPa) [20].

The trend of the Young's modulus of the composites, irrespective of the methods of post-curing was the same. For the whole range of SLG by weight, the Young's modulus values of the microwave-cured samples were a little bit higher their counterparts. This is in line with the results obtained in this study in which microwave post-cured specimens have lower electrical and mechanical loss, which mean the material is stiffer with higher glass transition temperature. It can be argued that the mechanical properties obtained by performing tensile tests for microwave post-cured samples were, on the average, 14% higher than their

counterparts but the post-cured times were much less, 10 hours to 30 minutes, a reduction of 2000 % [19].

The addition of SLG to phenolic resin lowers the tensile strength and Young's modulus of the composites, irrespective of the post-curing methods. This can be explained by the fact that the interface between the SLG and the matrix (phenolic resin) is poor as depicted by Figure 8. In addition, some SLG particles have been removed from their original locations and only holes remain. Moreover, where the SLG remain, they exist as whole particles and are not broken, which means that there is a poor adhesion, poor interaction between the SLG particles and the matrix. The Young's modulus and tensile strength of the composites are therefore lower with increasing percentage by weight of SLG. Figure 9 provides a closer look at a more serious gap in which the SLG is totally not interacting with the matrix.

Figures 10 and 11 show the well distributed SLG particles in the matrix. They have been obtained from two different samples with percentages by weight of SLG of 20 and 30% respectively. They have also been taken from different parts of the test pieces.

Conclusion

From electrical loss tangent measurements, it was found that the microwave post-cured samples have lower loss tangents than their counterparts in lower frequency range. The main contributor to this phenomenon is the absence of or very little water molecules in the specimens because of higher degree of curing. It can be argued that the absence or very little molecules in the samples make the samples harder.

From mechanical loss tangent measurements, it was found that the microwave post-cured samples have higher storage moduli and the specimens should be harder. The absence or very little molecules in the composites make the sample harder.

From the above two arguments, it is fair to say that when the electrical loss tangent of a material is low, its storage modulus should also be low. The material is harder and has less or no water molecules. In the future, instead of measuring the dielectric loss tangent of a material to determine its suitability of microwave processing, one can measure its storage modulus. On the other side of the coin, instead of measuring its storage modulus to determine whether the material is soft or hard, one can measure its dielectric loss tangent.

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