THE DEVELOPMENT OF A DIELECTRIC SYSTEM FOR THE ON-LINE CURE MONITORING OF THE RESIN TRANSFER MOULDING PROCESS.

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SUMMARY

The aerospace industry has identified the need for an on-line cure monitoring system for the RTM process which can determine the through-thickness cure state of a composite, without affecting the integrity of the finished component. Several techniques have been extensively investigated but Dielectric Analysis (DEA) appears to offer the greatest potential. The parallel plate sensor configuration is appropriate for through-thickness measurements. Using a laboratory dielectric instrument, dielectric properties in fibre (conductive and non-conductive) reinforced composite samples have been measured during a simulated RTM cure cycle. Particular parameters derived from dielectric measurements have been shown to be indicative of key stages at which the resin must exhibit specific properties if optimum mechanical properties of the fully cured composite are to be achieved. Correlation of key dielectric events with other thermal data has been shown. Sensors are currently being developed with a view to eventual incorporation into the RTM mould. The ultimate aim of this work is the development of an on-line cure monitoring system for the RTM process in collaboration with Bombardier Shorts.

INTRODUCTION

Composite materials are on the increase in areas such as the aerospace and automotive industries. Composites are gaining wide acceptance because of their high strength to weight ratio and their ability to replace metals in many applications involving structural members. Now that composites are taking off, improving the cost effectiveness and achieving the optimum material properties in the manufacturing process are some of the challenges facing today's composites industry.

Composite processing has traditionally been by the autoclave or wet lay-up method, this having been qualified and validated in the aerospace industry for high quality composite components. Resin Transfer Moulding (RTM) has been developed over a number of years and allows the economical manufacture of high quality composites. In the aerospace industry the most visible advantage to this closed tool moulding process lies in its ability to make complex shapes.[1] For the application of this process to expand, composite components must be manufactured with similar or improved properties to those produced using the autoclave technique, and at a lower cost.[2 3]

Basically the composite is produced as a fabric impregnated with a matrix, in this case an epoxy resin. Heat is applied and the resin reacts chemically to produce a rigid crosslinked

structure; this is known as cure. The curing process has been shown to be the most critical and costly stage in the manufacturing of composite structures[4]. The aerospace industry desires a better understanding of the rheological and chemical changes occurring during the curing process within the whole component to enable manufacturing process optimisation.[5] A sensor which can determine the state of cure of a composite on-line, and at points remote from the surface, without affecting the integrity of the finished component is required.[6]

There are a number of techniques which have been investigated for cure monitoring but dielectric analysis appears to be the most promising and popular method for monitoring the resin state in composites for control purposes.[7] The dielectric technique has existed for many years but only lately has the technology advanced to the point that its true potential is being recognised.[8] A wider application of the technique has been inhibited by a lack of basic knowledge of the relationships between molecular structure and the macroscopic dielectric behavior.[9] Dielectric Analysis is a sensitive technique for characterising many of the key properties of a polymeric material providing quantitative thermal, rheological and dielectric information on a wide range of materials in their different forms. The basic dielectric principles can be found in other literature.[10 11]

There are basically two types of sensor configuration for dielectric analysis. The "comb" or interdigited design, which has had some commercial success with Micromet Instruments[12 13 14] and the Frequency Dependent Electromagnetic Sensor (FDEMS) by Kranbuehl [15 16 17] have both been successfully used for the on-line cure monitoring of the RTM process.

These sensors types both suffer from a number of limitations. In particular their very localised region of measurement is considered a major limitation. Industry has identified two related problems:

- At present, measurement through the thickness of a composite requires sensors to be placed at intervals within the layers.[18] When these sensors have been incorporated into aircraft components they have been shown to affect the mechanical performance of the final part.[19]
- Thermal spiking is a serious problem in the curing of thick composites.[20] This can result in uneven temperature distribution across the thickness leading to non-uniform curing. This non-uniformity in temperature history leads to a variation in the mechanical properties across the part thickness.[21] The parallel plate arrangement can be used to evaluate the bulk dielectric properties in a material as the sample is sandwiched between two non-invasive electrodes.

The following additional advantages are noteworthy:

- The parallel plate configuration has calculable cell constants and very high accuracy compared to other electric measurement techniques.
- Parallel plate data has been successfully correlated with data from existing thermal analysis techniques such as DSC and DMA, and with mechanical test data such as flexural and tensile strength.[22]

In order for the technique to progress from the laboratory to an industrial environment certain issues need to be addressed. Perhaps the most important of these is that a fundamental understanding of the relationship between the dielectric parameters and the chemistry and rheology of the system is essential. Correlations have generally been resin specific and have limitations which are not always clearly stated in the literature.

A recent government report stated that "the development of a dielectric sensor and the associated instrumentation and software by which to monitor accurately the changing properties of a curing polymer matrix resin has become an urgent requirement in order to facilitate the many advances recently made in cure modelling etc."[23]

EXPERIMENTAL

The research conducted at the Engineering Composites Research Centre (ECRE) has focused on these problems encountered in the aerospace industry and is concentrating on the development of an on-line cure monitoring system for the RTM process in collaboration with Bombardier Shorts. The work has involved accurately simulating the RTM process using a laboratory dielectric instrument. The RTM process involves several key stages at which the resin must exhibit specific properties to ensure the composite part achieves optimum final mechanical properties. These stages in the curing reaction have been identified by appropriate dielectric signals and correlated with other established thermal analysis techniques.

Previous research has shown that it is possible to accurately simulate the RTM process for 4 layers of glass and carbon fibre impregnated with an epoxy resin. Cure times corresponding to given values of a chosen dielectric signal were obtained and a correlation was demonstrated between DEA, DSC and DMA as well as static room temperature mechanical test data.[24] The analysis of carbon fibre composites by dielectric analysis is extremely important for the aerospace industry.

Due to the conductivity of the carbon a suitable insulating layer had to be found to insulate the electrodes and provide minimal disruption to the dielectric signal. A polyimide film was chosen as it possessed a number of unique properties which make it ideal for this application. The most important of these is that the film has a low, fairly constant dielectric response over the temperature and frequency ranges of interest. A film thickness of 75μm was chosen as this was shown to be sufficiently robust to reliably insulate the sample but not too thick to attenuate the signal significantly.

The dielectric instrument was operated in the parallel plate configuration under an inert atmosphere. The instrument was calibrated before each run to check the sensor alignment, temperature profile and the electrode sensing area overlap. A load of 300N was applied to the DEA sample to ensure good sensor contact, maximise the fibre volume fraction in order to achieve comparable levels to those from the RTM and to minimise the presence of voids. Data was collected and analysed using the TA DEA Data Analysis V4.2a Software.

The matrix system was an epoxy resin supplied by CIBA Polymers. This is a two part system of LY-564 resin and HY-2954 hardener suitable for RTM and hand lay-up applications. 4 layers of carbon fibre plain weave were analysed in the dielectric instrument.

A temperature programme was set up to simulate that of the RTM process plus the subsequent postcure cycle. The resin was degassed for 1 hour at 30°C prior to testing.

DEA Method
Step1: Step increase to 75°C
Step2: Isothermal for 6minutes
Step3: Ramp 0.64°C/min to 100°C
Step4: Isothermal for 60minutes
Step5: Step increase to 145°C
Step 6: Postcure isothermal for 1000minutes.

CORRELATION

It is extremely important that any technique developed for cure monitoring be correlated with existing established techniques and validated in a particular industry. In this case the aerospace industry will want to know the potential benefits of the new method and the cost. It also needs to be able to convince the Aviation Authorities of the validity of the results.

Dynamic Mechanical Analysis (DMA) measures the properties of materials as they are deformed under periodic stress and is widely regarded as an extremely important tool for characterising the viscoelastic properties of materials. DMA is used in this instance for the determination of gelation of the neat epoxy resin. The test method was supplied by Bombardier Shorts.[25] The test procedure meets or exceeds existing national and/or international standards and is based on CRAG Method 1100. The instrument utilised for this work was a DMA 983 fitted with the low mass clamps. The neat, degassed resin was placed in an aluminium foil "boat" to a depth of 5mm. A metal paper clip was clamped in the driven arm and attached so that it penetrated the surface of the resin by approximately 2mm. The instrument was set up to simulate the RTM cure cycle as in the dielectric instrument. The instrument was used at a fixed frequency of 1Hz with an oscillation amplitude of 1.50mm.

The parameter that is most sensitive to the advancement of the cure process and indicative of the thermoset network density is the glass transition temperature Tg. The fact that Tg increases non-linearly with the degree of cure makes it more sensitive in the later stages of the cure.[26] There are many techniques for the determination of Tg but this experimental work has focused on Differential Scanning Calorimetry (DSC). DSC is used to determine the rate and extent of reaction for thermoset resins. DSC measures the temperature and heat flow associated with transitions in materials as a function of temperature and time. Resin only samples were analysed by DSC to determine the Tg. The instrument was programmed to simulate the RTM cycle but stopped at appropriate postcure times. The sample was then reanalysed at a heating rate of 10°C/min to determine the Tg.

RESULTS AND DISCUSSION

Dielectric analysis measures the two fundamental electrical characteristics of a material, the conductance and the capacitance as a function of time, temperature and frequency. These electrical properties are important but are even more significant when correlated to activity on a molecular level. May et al.[27] showed that changes in the dielectric properties of a curing resin can be related to the salient chemical and rheological events of the process.

During the RTM process the resin undergoes several important transitions. As the resin is introduced into the RTM tool the viscosity must fall low enough to ensure the best possible

wet out of the fabric structure, and achieve maximum penetration into the yarns. If this does not occur the result can be a low fibre volume fraction and the presence of voids, leading to a reduction in the mechanical properties. In relation to dielectric analysis there are several parameters which have been shown to indicate the minimum viscosity. However the ionic conductivity has been identified as an extremely useful dielectric parameter because it can be directly related to the viscosity.[28] The direct relationship between viscosity and ionic conductivity can be readily understood when it is noted that the latter is essentially a measure of the ease with which ionic impurities can migrate through the resin. For epoxy resins, it has been suggested that sodium and chloride ionic impurities, whose concentration remains constant during the experiment, are the species which dominate ionic conductivity.[29 30] On Fig 1, a plot of the ionic conductivity versus cure time (frequency 1000Hz) there is a clear peak. At this frequency the signal proved to be clean and thus required minimal smoothing (2 on a scale of 0-10). Low frequencies have been shown to be the most accurate for the onset of cure but problems occur due to polarisation and blocking effects. Blocking results from polarisation in the sample and is further exacerbated by the presence of an insulating film. A generic rule for dielectric properties states that the maximum in the resin conductivity coincides with the point of minimum viscosity under isothermal or dynamic (thermal) conditions.[31] From Fig 1 the minimum viscosity occurs after 19 minutes.

The second important stage in the resin cure process is known as gelation, where curing of the matrix becomes predominant. Gelation marks the first appearance of the crosslinking reaction and the gel point is a key characteristic of the resin. A further generic rule relating ionic conductivity to initiation of gelation has been stated thus; "the inflexion point in the drop of the logarithmic ionic conductivity after the point of maximum flow provides the first evidence of a gelled material."[31]

A point of inflexion is defined as a point at which $\frac{d^2(LIC)}{dt^2} = 0$

where LIC is the log of the ionic conductivity. The software does not allow the determination of the second derivative of the LIC with respect to time but can provide the first derivative known as DLIC (derivative of the log of the ionic conductivity). A point of inflexion is located by a zero slope on the DLIC versus time curve (see Fig 2). The first point of inflexion following the maximum resin conductivity is taken as the onset of gelation (25minutes on Fig 2).

As mentioned correlation of these parallel plate DEA results with established, validated data is essential. The DMA resin "boat" is utilised to indicate gelation of the neat resin. It has been widely reported in the literature that the point at which tan δ=1 corresponds to the gel point.[32] In Fig 3 it can be seen that tan δ=1 at a time of 34minutes. The corresponding time determined using DEA as described above is 25minutes. This apparent discrepancy led to a comparison of the temperature-time profiles in the two experiments. It was discovered that the DMA profile lagged the DEA profile by approximately 10minutes. Thus the corrected time for DMA is 34-10=24minutes. The correlation between DEA and DMA indicators of gel point is therefore very good. At a corrected DMA time of approximately 15 minutes, it is suggested that the minimum value of E", the loss or viscous modulus, indicates minimum viscosity which correlates relatively well with the dielectric trace in Fig 1, the indication of minimum viscosity by DEA.

After gelation there is progressive formation of the molecular network resulting in a substantial increase in the crosslink density, glass transition temperature and the mechanical properties. Vitrification follows gelation and occurs as a consequence of the increasing average size of the molecules and by the network becoming tighter through crosslinking.[33] The Tg will continue to rise until it is similar to the isothermal cure temperature. When the Tg is similar the resin is said to have vitrified so the resin is now in a glassy state. The material, now solid, will exhibit very slow curing indicating the end of cure with the Tg becoming slightly higher than the isothermal cure temperature. Further curing will result in degradation and a loss of mechanical properties. Resin only samples were analysed for a number of reasons. They were shown to be an accurate representation of the carbon reinforced composite prepared by the RTM procedure. The thermal cycle by DSC was shown to be extremely accurate giving well defined glass transitions and the results showed considerably less variation than those obtained on RTM plaques postcured to the same times. DSC is used to determine the increase in the degree of cure by an increase in the Tg until it is similar to the isothermal cure temperature, in this case 145°C. The cure time associated with the highest Tg value signifies when the composite is fully cured and the mechanical properties are at their optimum.[34] (see Fig 5)

DLIC is considered to be an indicator of the rate of cure. The first part of the curve in Fig 4 shows a reducing rate of cure, presumably due to increased crosslinking, followed by a plateau. It is postulated that vitrification occurs within this plateau region, based on comparative DSC data shown in Fig 5 (time at which Tg=145°C). The precise location of vitrification cannot at this time be ascertained due to insufficient DSC data. This plateau is then followed by a phase in which a reducing rate of cure is again evident. Within this region it is suggested that full cure occurs. This again is based on DSC data (Fig 5), full cure being indicated by the maximum value of Tg. The paucity of data in this area is evident and at this stage precludes more precise location of the full cure point. The final phase shown in Fig5 is another plateau which represents a constant and very small cure rate.

CONCLUSIONS AND FURTHER WORK

Research has identified and focused on problems encountered in the aerospace industry for the RTM process.

- The dielectric instrument, operated in parallel plate configuration has been used to identify important transitions in the resin, namely minimum viscosity, gelation, vitrification and full cure, which ultimately affect the final mechanical properties of the composite. An operational frequency of 1kHz was found to be the most sensitive for identification of all these parameters.
- The technique has been applied to composites containing conductive fibres.
- Correlations have been demonstrated between dielectric results and other established thermal analysis techniques.

Currently research is continuing to correlate the dielectric response with other thermal and mechanical test techniques. A different resin system will also be examined. Insulated parallel plate sensors are being developed for in tool monitoring.

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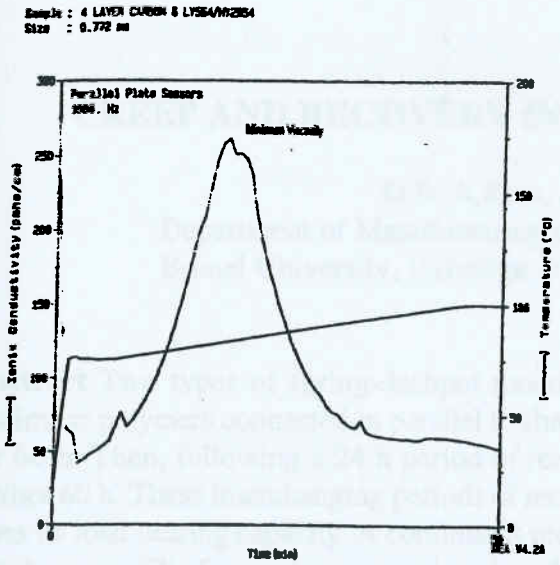

Figure1:Dielectric Trace Showing Minimum Viscosity

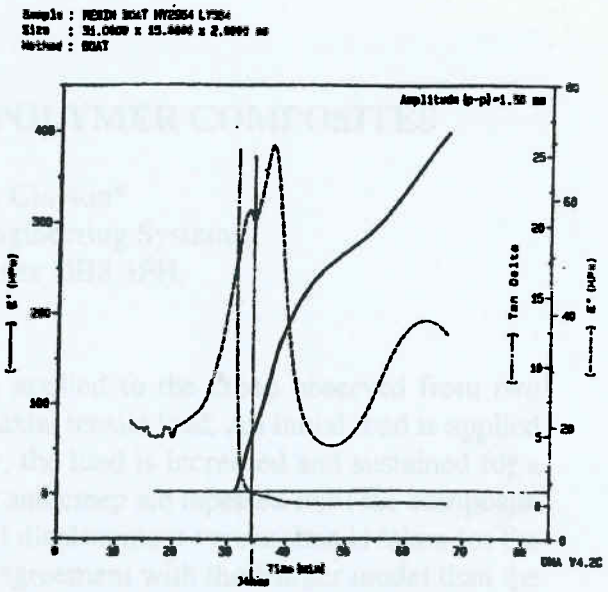

Figure3:DMA Trace Showing Gelation

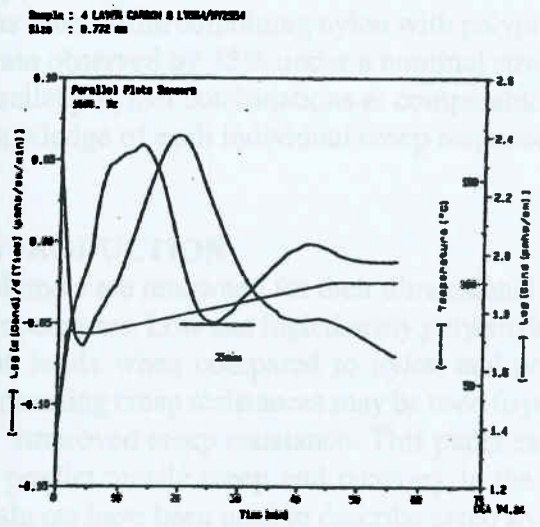

Figure2:Dielectric Trace Showing Gelation

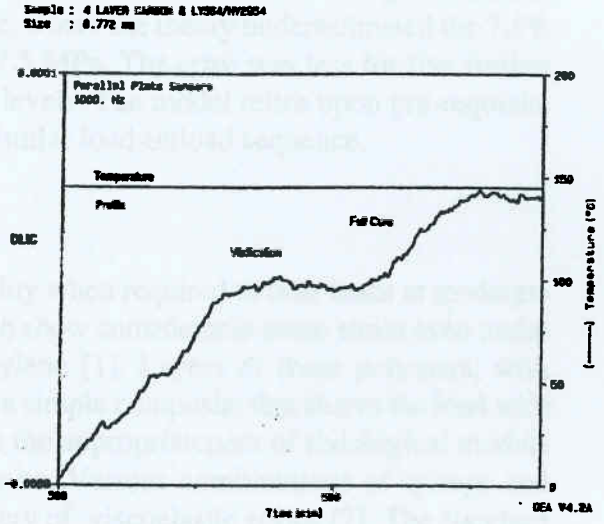

Figure4:Dielectric Trace Showing Vitrification and Full Cure

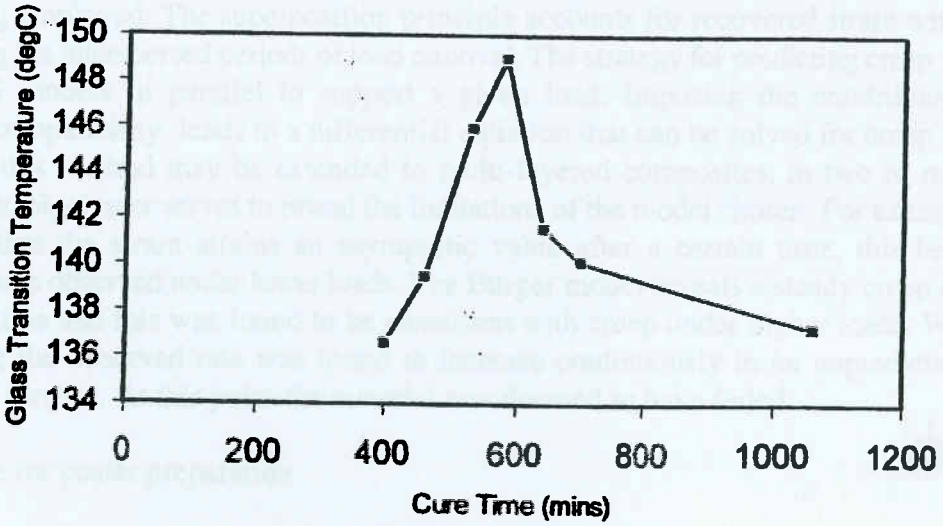

Figure5:Graph Showing Tg versus Cure Time