

Prior Thermal Spikes and Thermal Shocks on Mechanical Behavior of Glass Fiber-epoxy Composites

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ABSTRACT

Fiber reinforced glass-epoxy composites with and without prior thermal history were subjected to hygrothermal conditioning for different exposure times. The prior thermal history was given in form of thermal shocks and thermal spikes at three different temperatures. The effects of exposure time and prior thermal history on the moisture absorption kinetics were studied. The effects of prior conditioning parameters were also investigated. The variation of mechanical properties as a function of exposure time and prior conditioning parameters were assessed by the three-point short beam shear bend test. It has been observed that there is an initial improvement in the mechanical properties followed by a steady deterioration. Mechanical tests performed at different crosshead velocities showed increasing brittleness of the composites and that was found to be a function of crosshead velocity.

KEY WORDS: polymer-matrix composites, Environmental degradation, Mechanical properties, hygrothermal behavior

INTRODUCTION

Fiber-reinforced plastics (FRPs) are increasingly becoming the preferred structural materials for a variety of applications including ground-based and air-borne vehicles, space structures and sporting goods [1]. An aircraft structure may often be subjected to kinetic heating during its flight [2,3]. In such situations it becomes imperative to understand the mechanical response of the composite structures under hygrothermal environments. Common prior conditioning effects in these cases are the presence of thermal history in form of a thermal spike or a thermal shock. In hot and humid conditions, FRP composite absorb moisture. Moisture absorption causes swelling of the polymer, giving rise to hygroscopic stresses. Presence of thermal spikes and thermal shocks lead to development of thermal stresses. The presence of these stresses can result in matrix cracking. In an FRP composite, the fiber and the matrix have different coefficients of thermal expansions (CTE). Hence, excursions through the same temperature range results in differential expansion. This induces additional stresses at the fiber-matrix interface, thereby weakening the interfacial region. This can result in debonding and ultimately delamination of the composite by interfacial failure. The shrinkage undergone by the composites during curing lead to curing stresses. The degree of cross-linking may increase during thermal conditioning. The high cross-linked networks have lower molecular mobility. Consequently, the mechanical behavior of these composites is different from the composites without any form of thermal conditioning [4]. The state of the composites becomes even more complicated due to the loading conditions during its usage. The variation in strain rates during performance induces different degrees of brittleness in the matrix. The coupled interactions of these factors lead to deterioration of mechanical properties and subsequent fracture. The fracture resistance of FRP composites can be explained on the basis of elongation of fibers. They elongate in a stepwise manner as folded domains or loops are pulled open. The elongation events occur for forces of a few hundred piconewtons which

are less than forces of a few nanonewtons required to break the polymer backbone in the threads. The molecular elongation looks to be the key reason for toughness [5].

The present focuses on the effect of prior thermal history on the hygrothermal behavior of glass-epoxy composites. The thermal history is introduced by giving thermal spikes and thermal shocks to different batches of FRP composites at three different temperatures, namely 100, 150 and 200°C. We observed that the interlaminar shear strength (ILSS) showed a general decline with increasing exposure to a hygrothermal environment irrespective of the thermal history. However the rate of deterioration seems to be more pronounced for specimens with a thermal history as compared to the specimens without any thermal history. The objective of the present work is to study the hygrothermal behavior of FRP composites with either improved or weaker interfacial adhesion.

EXPERIMENTAL

The materials used for the current investigations comprised of E-glass fiber woven roving having a density of 0.36 kg/m² and epoxy adhesive (Ciba-Geigy, India, LY-556 araldite, HY-951 hardener). The FRP specimens were fabricated using the conventional hand lay-up method. A releasing sheet having non-stick properties with respect to the laminate was placed on a plane mould. A layer of catalyzed epoxy resin was poured on it uniformly. Light rolling was then carried out to remove the air pockets and distribute the resin uniformly through out the composite. A sixteen layered structure was thus prepared which was then allowed to harden upon curing. After the composite sheet was cured, it was cut into smaller three-point bend test specimen dimensions as per the ASTM specifications using a diamond tipped cutter.

The specimens were divided into seven batches. The first three batches were given thermal shocks at temperatures of 100, 150 and 200°C. Thermal shocks involved sudden

exposure of the specimens at an elevated temperature for ten minutes followed by quenching in ice-water. The next three batches were given thermal spikes at temperatures of 100, 150 and 200°C. Thermal spikes were given by sudden exposure of the specimens at elevated temperatures for ten minutes followed by slow cooling (in form of furnace cooling). The last batch was not given any prior thermal history.

After the initial conditioning the specimens were hygrothermally conditioned in a humidity cabinet where the conditions were maintained at 60°C and 96%RH. The humidity cabinet had a inbuilt thermometer and hygrometer for humidity and temperature measurements. The temperature variation was maintained between 0.5°C whereas the RH variation was allowed in the 0-1% range. The composite laminates were placed on perforated trays. The hygrothermal conditioning was carried out for different lengths of time.

The three-point bend tests were then carried out for the composite specimens. Carry was taken to allow the same relaxation time prior to testing. The tests were performed with an Instron 1195 testing machine. The tests were performed on different specimens at crosshead velocities of 2mm/min, 10mm/min and 50 mm/min. The interlaminar shear strength was ascertained as follows

$$ILSS = \frac{0.75P_b}{bd} \quad (1)$$

Where P_b = breaking load

b and d are width and thickness of the specimen respectively.

RESULTS AND DISCUSSIONS

Figure 1 shows the generalized moisture absorption curve for glass-epoxy composites in the present experiment. The moisture absorption is a function of time [6]. The plot shows three distinct regions. The first region shows a marked linearity. This is in accord with the solution of Fick's second law, and may be regarded as the Fickian region, where the Fickian moisture kinetics is followed. Following this, a plateau like region is reached. This indicates a

saturation level being reached. The amount of moisture pick up is a function of the partial pressure of the moisture in the surrounding and the moisture in the composite. Once a temporary equilibrium is reached we get a saturation region. Prolonged exposure to hygrothermal environment results in the third stage of the curve. The prior thermal history, whether shock or spike, may induce crazing and cracking. On prolonged exposure at elevated temperature the interactions of the various stresses present in the matrix results in enhanced cracking. These cracks further widen up thereby providing fast diffusion paths for the moisture. This is enhanced by the presence of temperature, which as such acts as an activator [7]. The moisture uptake in this case is strongly dependent on the rate of widening of the cracks. The growth of matrix cracks depend on a variety of stresses like hygroscopic stresses, curing stresses and residual thermal misfit stresses during prior thermal conditioning apart from the individual material properties of the fiber and matrix. The complexity of these interactions may result in non-linear crack growth. The moisture pickup kinetics depend pathways available in form of cracks. Hence non-Fickian crack growth results in a non-uniform rate with which new routes are available for moisture pick up, thereby exerting a non-linear effect. This culminates in non-Fickian kinetics governing the moisture pickup. This is indicated by the rather wavy nature of the curve. The flattening refers to the period when the cracks are slowly opening up. Another phenomenon which may be responsible for the flattening is microcracks coalescence whereby the cracks coalesce upon prolonged exposure due to a net compressive nature of the residual stresses developed largely as a consequence of the interaction of the curing stress, hygroscopic stress, the thermal stress and the matrix plasticity stresses. The steep hike in the curve refers to the period when the cracks have opened up sufficiently to allow accelerated moisture pick up. The combination of these two opposite phenomenon may be responsible for the wavy nature in the non-Fickian region.

Moisture can penetrate into the FRPs through capillary action at the fiber/matrix interface, through the cracks and voids and through the resin by diffusion [8,9]. Initially

moisture absorption starts at the interface between the polymer matrix and moisture laden environment. The microvoids created due to polymerization of polymer chains are prime sites for moisture pickup. The moisture first diffuses into these microvoids and then dissolves into the matrix. Gradually the moisture reaches the fiber-matrix interface. The adhesion at the fiber-matrix interface is due to bonding of physical, chemical as well as physicochemical method. Amount of moisture absorbed by the epoxy matrix is significantly greater than fibers which absorb little or no moisture [10]. This results in significant mismatch in moisture induced volumetric expansion between matrix and fibers leading to the development of stress and strain fields in the interfaces of composites. Thus, due to moisture absorption, the hygroscopic stresses are introduced. The hygroscopic stresses result in weakening of the mechanical bonds, although in some specific cases there may be some strengthening, depending on the nature of the complex interactions with other stresses like thermal and curing stresses. Additionally, moisture absorption leads to changes in thermophysical, mechanical and chemical characteristics of the epoxy matrix by plasticization and hydrolysis [10]. These changes decrease the glass transition temperature (T_g) and elastic modulus. At the same time, the moisture wicking along the fiber-matrix interface degrades their bond. It has been shown that during absorption, the outside ply of a composite laminate is in compression [11]. This results from the outer ply trying to swell, but being restrained by the dry inner plies. This results in tensile stresses in the outer plies. The net effect of moisture absorption is deterioration of matrix dominated properties such as compressive strength, interlaminar shear stress (ILSS), fatigue resistance and impact tolerances (this is evident from Woehler curves before and after wet conditioning) [10]. This results in decrease of damage tolerances and long-term durability. At the chemical level, the presence of moisture provides a polar group, which may replace the fiber-matrix bonds thereby adversely affecting the interface adhesion chemistry. A combination of these processes occurs in case of alteration of physicochemical nature of fiber-matrix bonding.

It is generally assumed that the changes in diffusion characteristics are caused by cracks which develop due to temperature induced stresses. Thermal treatment can significantly alter the properties of the material [12]. The fiber and the matrix have different CTEs. Hence, sudden exposure to high temperatures results in differential expansion of the fiber and the matrix. This sets up tensile stresses at the interfacial regions resulting in partial debonding [13]. As a result, interior of the laminate is accessible to the wetting during subsequent hygrothermal conditioning [8]. The properties of FRPs, however, degrade not only at higher temperatures, but at temperatures less than room temperature as well. This is due to the increased brittleness of the materials [14,15]. The thermal conditioning at slightly high temperature may also result in post-curing and strengthening. The post-curing effects may be due to further polymerization in the epoxy matrix and may also induce more adhesion at the interface. The thermal conditioning may change the chemistry of the fiber-matrix interface in forming an interpenetrating network and also improve the adhesion at the interface either by mechanical interlocking or by a surface chemistry mechanism.

The nature of the prior thermal treatment has a strong correlation with the moisture pickup kinetics in the composite laminate. Figures 2 and 3 show the effect of the prior conditioning type, whether shock or spike, on the moisture pick up by the composite specimens. The moisture uptake is higher in case of shocks than in case of spikes. This may be explained on the basis of the post-curing polymerization which leads to cross-linking. During this process the polymer chains get tangled and hence results in creation of larger number of interconnected voids. The number of voids being of greater importance than the actual volume, moisture sorption is more. As shocks provide less time for cross-linking, the anomaly in moisture pick up is explained.

The hygrothermally conditioned specimens without any thermal history showed the highest moisture pick up kinetics. This indicates that thermal excursions at relatively lower temperatures are not effective in weakening the interfacial bonding. The greater degree of

dominance of moisture absorption kinetics in hygrothermally conditioned specimens over the other two cases at 100°C as compared to 200°C further strengthens this line of thought. Studies by various investigators have also shown that a single thermal excursion is often not very damaging, provided the temperature is not very high [2]. At higher temperatures of shocks or spikes, an anomaly occurs, with spikes showing higher moisture pick up rates. Predominance of spikes at higher prior conditioning temperatures may be due to the fact that cross-linking is a temperature dependent phenomenon which is favored at higher temperatures. Higher cross-linking leads to larger number of voids, which provide a more active pathway for moisture. Greater cross-linking reduces the molecular mobility over a localized region. This is likely to result in a shift of the glass transition temperature above its normal temperature and induce a greater brittleness in the matrix. The formation of newer bonds due to the post-curing effects can result in strengthening of the composite laminate. A deleterious effect of sudden high temperature exposures arises due to the significant difference in CTEs of the fiber and the matrix which may bring about delamination. Moisture absorption may take place along the debonded areas by capillary action, thereby enhancing the absorption kinetics.

The moisture sorption kinetics is dependent on the prior conditioning temperature. Figure 4 and 5 show the effect of the prior conditioning temperature on the moisture pick up behavior of the glass-epoxy composites for prior shocks and spikes respectively. The changes in diffusion characteristics, when shocked or spiked to different temperatures, are caused by cracks which develop due to temperature induced stresses. Due to differential coefficients of thermal expansion, the fiber and the matrix tend to expand up to different extents, thereby setting up misfit strains in the composite. This is more pronounced for shocked specimens because of the rapid cooling involved. This further weakens the bonds, especially the physical bonds at the interfaces. Consequently, more number of active pathways are available for the moisture to enter. Also the chance of fiber wetting by moisture is greater resulting in

enhanced disparity exists for specimens conditioned at different temperatures for shocked composites. Thermal spikes can significantly alter the properties of the material [12]. The polymerization reactions are temperature dependent phenomena. Spiking at higher temperatures offer much more chance of cross-linking and further polymerization, thereby creating microvoids through which moisture can diffuse. The presence of moisture results in swelling stresses. Spikes may modify the threshold stresses required for delamination of the inner plies due to the differential CTEs of the fiber and the matrix. Greater is the conditioning temperature the wider is the temperature range experienced by the composite and more is the degree of mismatch in expansion / contraction of the fibers and the matrix resulting in deadhesion at the interface. This accounts for the enhanced damage at higher temperatures. As a result, interior of the laminate is accessible to the wetting during subsequent hygrothermal conditioning [8] and this further abets the moisture pickup.

The interlaminar shear strength (ILSS) gives a very good idea regarding the fiber-matrix adhesion strength. The ILSS reflects the resultant of a variety of factors towards the fiber/matrix adhesion possibly including secondary bonding, residual compressive stresses arising during thermal treatments, mechanical locking friction, curing stresses and hygroscopic stresses [9]. The three-point bend tests were performed so as to assess the mechanical behavior during severe environmental exposure of the composites. The interlaminar shear strength increases initially for epoxy matrix composites and then decreases gradually. Towards the end a hump appears. The ILSS plots are a reflection of the complex stressed state of the composite, with the key stress components being the swelling or hygroscopic stresses, thermal stresses, initial curing stress and in some cases the stress associated with post-curing or further polymerization. The effects of thermal treatments are then twofold. On one hand, polymerization reactions involve formation of newer bonds while the presence of residual thermal stresses and enhanced hygroscopic stresses due to crack

assisted moisture pick up result in deadhesion at the interface and decohesion of the polymer matrix. The mechanical behavior is the resultant of these opposing effects.

Figures 6 and 7 show the effects of the type of prior thermal treatment on the ILSS of the composites at two different crosshead velocities. It can be seen clearly that the plots show an initial increase in the values of ILSS. This is a manifestation of post curing effects and cross-linking due to the high temperature excursions. Since spiked specimens get to spend more time at high temperatures, it is likely that greater degree of post curing occur in this case. Therefore they show a marked difference in the initial increase with respect to the shocked specimens for different prior conditioning temperature. The thermal conditioning at slightly high temperature may result in post curing and strengthening. The post curing effect is due to further cross-linking in the epoxy matrix and induces greater adhesion at the interface due to the formation of an interpenetrating network. The thermal conditioning changes the chemistry of the fiber-matrix interface in forming an interpenetrating network and also improves the adhesion at the interface either by mechanical interlocking or by a surface chemistry mechanism. It is well known that post curing depends largely on the temperature and time, and this fact is manifested in the ILSS plots.

Effect of thermal shock definitely causes debonding and/or weakening of interface because of the different thermal coefficients of expansion/contraction of the polymer matrix or fiber reinforcement [13]. The ILSS plots at different crosshead velocities also show a similar trend.

Thermal shocks, when compared to spikes offer more scope for thermal stresses and consequently debonding leading to interfacial weakening and delamination. Spikes, on the other hand, provide greater opportunities for post curing effects especially in the epoxy matrix composites, thereby bringing about an improvement in the ILSS. For spiked specimens, some water molecules can remain entrained in the polymer up to 180°C. This could be due to thermally activated process at higher temperatures leading to chain scissions [16]. The results

indicate that thermal spiking induces relaxation of polymer network. This explains the lower ILSS values obtained for shocked specimens as compared to spiked specimens.

The prior conditioning temperature also influences the degradation kinetics of the composites. Figures 8 and 9 show the effects of prior thermal conditioning temperature for a given thermal history in composite specimens. The maximum values of ILSS for shocks or spikes are observed at 200°C and minimum for 100°C. This is seen in the initial period only. With increasing conditioning time, the strength for specimens conditioned at higher temperatures show a more rapid deterioration. A careful examination leads to the conclusion that these curves can be divided into three stages. The first stage shows a dominance of spiked specimens. The post curing effects contribute heavily to this. The second stage shows spiked and shocked specimens on an equal footing. At this stage, the hygroscopic swelling stresses tend to neutralize the initial curing stresses, although the effect of thermal degradation remains. As spiked specimens absorb more moisture also, there lies a possibility of moisture accumulation at the interface leading to interface weakening. This largely counteracts the positive effects of post curing strengthening in case of the epoxy composites. The final stage sees a drop in the value of ILSS for all three specimens with all the three curves reaching similar values. Evidently over a long period, a severe thermal history can have adverse effect on the bulk strength of the material.

Figure 10, 11 and 12 show the effect of crosshead velocities on the hygrothermally conditioned specimens without any prior thermal history, with a history of shock and a history of spike respectively. The effect of varying crosshead velocity is to induce different degrees of brittleness in the matrix. Higher crosshead velocities imply less time for matrix to absorb the energy input during loading. This results in the matrix losing its damping properties. Hence, the loading energy cannot be dissipated as it would otherwise be at lower loading rates. Higher crosshead velocities also prevent proper load transfer in the composite. This has two effects. The first effect is that the fibers take most of the load, and the matrix doesn't play

as significant a role as it does for lower crosshead velocities. This contributes to the higher apparent strength of the composite as is indicated by the higher ILSS values. Secondly, improper load transfer affects the fiber-matrix interface. The net effect is enhanced brittleness. The composite, in effect, behaves like a rigid beam [17], which breaks upon rapid loading without much macroscopic deformation.

Figure 13 shows the scanning electron micrograph of a composite specimen with a prior thermal shock at 200° C after 16 hours of hygrothermal aging. The thermal spike coupled with hygrothermal aging has resulted in a distinct matrix crack. Figure 14 shows the scanning electron micrograph of a hygrothermally aged composite specimen without any prior thermal history. The absence of thermal history results in absence of misfit stresses. Hence the debonding at the fiber-matrix interface is not very highly pronounced. Here the hygrothermal stresses, which are tensile in nature gain prominence, while deadhesion between the fiber and the matrix is lower as compared to the composites with a prior thermal history. This results in a “tear” in the matrix. Figure 15 isolates the effect of prior thermal treatment in form of a thermal shock at 100° C. Clearly, the initial thermal shock causes deadhesion at the fiber-matrix interface. This is evident by the presence of an outcrop of naked fibers from the matrix. The matrix also tends to form a large number of cross-links and shrinks resulting in a slight coagulation of the polymer. Figure 16 shows the effect of high temperature prior thermal treatment in form of a shock at 200° C. The matrix damage in form of cracks is much more prominent here. Also, a clear deadhesion has occurred at the fiber-matrix interface. A comparisons of figures 15 and 16 clearly shows the role of temperature in causing interfacial damage in the composites.

Moisture absorption in epoxy matrix composites can take place through the fiber-matrix interface, cracks and voids in the composites and by diffusion through the resin [8]. The moisture distribution inside the material never attains a steady state. It changes continuously, the concentration depending on time and position [18]. Presence of high

temperature may lead in further matrix cracking, and this in turn accelerates the moisture pick up. Thus the prior conditioning temperature contributes to degradation of mechanical properties in two ways. First, the direct effect of prior high temperature excursions is to cause matrix damage in form of cracks. Second, the indirect effect of prior thermal history is to provide active pathways for fluid sorption, which in turn causes hygroscopic stress induced damage.

The level of adhesion between fibers and matrix affects the ultimate mechanical properties of composite-both parallel to direction of fibers as well as off-axis [11]. Shear failure in the interphase could be caused by interfacial shear failure between the fiber and interphase itself [10]. For a weak interface, interfacial shear failure occurs before interphase shear failure, and the maximum interphase shear stress at the time of debonding is treated as the interfacial shear strength and vice versa.

CONCLUSIONS

The effects of prior thermal history on the hygrothermal behavior of glass-epoxy composites have been assessed here. Thermal spikes provide more opportunities for post curing and cross-linking. The thermal stresses developed in case of spikes are lesser as compared to the shocks because of the gradual cooling. This accounts for the better ILSS in case of specimens with prior thermal spikes rather than shocks. Shocks create more of matrix cracking resulting in faster moisture diffusion.

The degree of cross-linking is a function of temperature. Higher temperatures lead to greater cross-linking. This can result in strengthening of the laminate. Greater exposure times offer more time for moisture absorption and it results in a general deterioration of mechanical properties. This could possibly account for the initial strengthening at lower exposure times, where the beneficial effects of thermal conditioning outweigh the detrimental effects of moisture absorption. Higher temperature leads to more of matrix cracking. This leads to more

number of fast diffusion pathways for the moisture thereby leading to accelerated moisture pick up kinetics. In general, the ILSS decreases with conditioning time, apart from the initial increase. Prolonged exposure creates a high degree of hygroscopic stresses which may result in microcracks coalescence and crack blunting leading to a marginal improvement in ILSS. With greater exposure time, there is in general an decrease in ILSS, while the moisture absorption kinetics change over from Fickian to Non-Fickian.

At higher crosshead velocities, the ability to absorb energy during loading decreases, even as the matrix changes over from ductile to brittle. Consequently, while the breaking load increases, the strain to failure decreases, and the glass transition temperature increases. It may be stated that the glass fiber-reinforced polymer composites seem to be synergic to environmental degradation by moisture pick up especially if they have a prior thermal history. The mechanical behavior of the glass-epoxy composites are reflected by polymerization and / or depolymerization.

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Figure Captions

- Figure 1** A generalized moisture absorption curve for glass epoxy composites during hygrothermal conditioning
- Figure 2** Effect of the nature of prior conditioning treatment at a constant prior conditioning temperature of 100° C
- Figure 3** Effect of the nature of prior conditioning treatment at a constant prior conditioning temperature of 200° C
- Figure 4** Effect of the prior conditioning temperature on the moisture absorption kinetics of shocked composites
- Figure 5** Effect of the prior conditioning temperature on the moisture absorption kinetics of spiked composites
- Figure 6** Effect of type of thermal treatment on degradation kinetics for composites treated at 150°C and tested at a crosshead velocity of 2mm/min
- Figure 7** Effect of type of thermal treatment on degradation kinetics for composites treated at 200°C and tested at a crosshead velocity of 50mm/min
- Figure 8** Effect of prior conditioning temperature on degradation kinetics of shocked composites at a crosshead velocity of 2mm/min
- Figure 9** Effect of prior conditioning temperature on degradation kinetics of spiked composites at a crosshead velocity of 2mm/min
- Figure 10** Effect of crosshead velocity on the interlaminar shear strength of hygrothermally conditioned glass-epoxy composites
- Figure 11** Effect of crosshead velocity on the interlaminar shear strength of hygrothermally conditioned glass-epoxy composites shocked at 100° C
- Figure 12** Effect of crosshead velocity on the interlaminar shear strength of hygrothermally conditioned glass-epoxy composites spiked at 200° C

- Figure 13** Scanning electron micrograph of a composite specimen with a prior thermal shock at 200° C after 16 hours of hygrothermal aging at a magnification of 300X
- Figure 14** Scanning electron micrograph of a hygrothermally aged composite specimen without any prior thermal history at a magnification of 380X
- Figure 15** Scanning electron micrograph of a composite specimen with a history of thermal shock at 100° C, prior to hygrothermal conditioning at a magnification of 380X
- Figure 16** Scanning electron micrograph of a composite specimen with a history of thermal shock at 200° C, prior to hygrothermal conditioning at a magnification of 500X

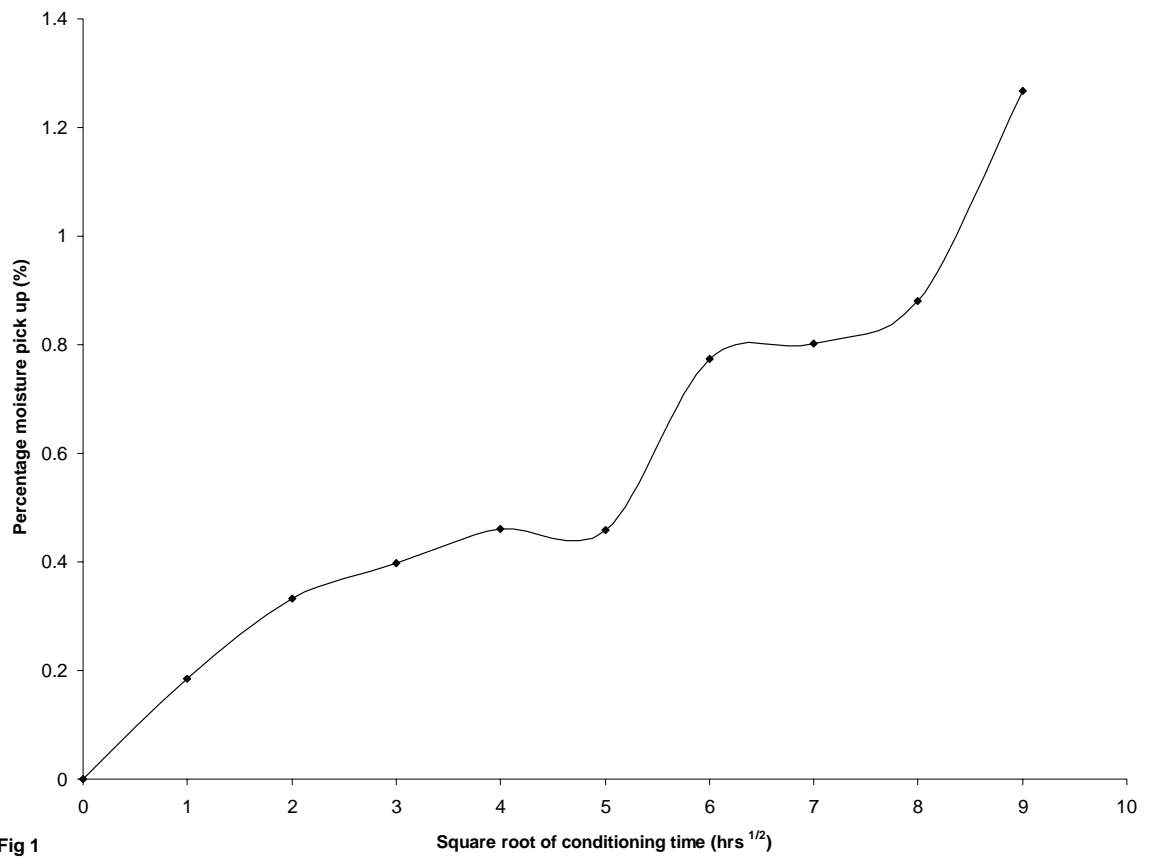


Fig 1

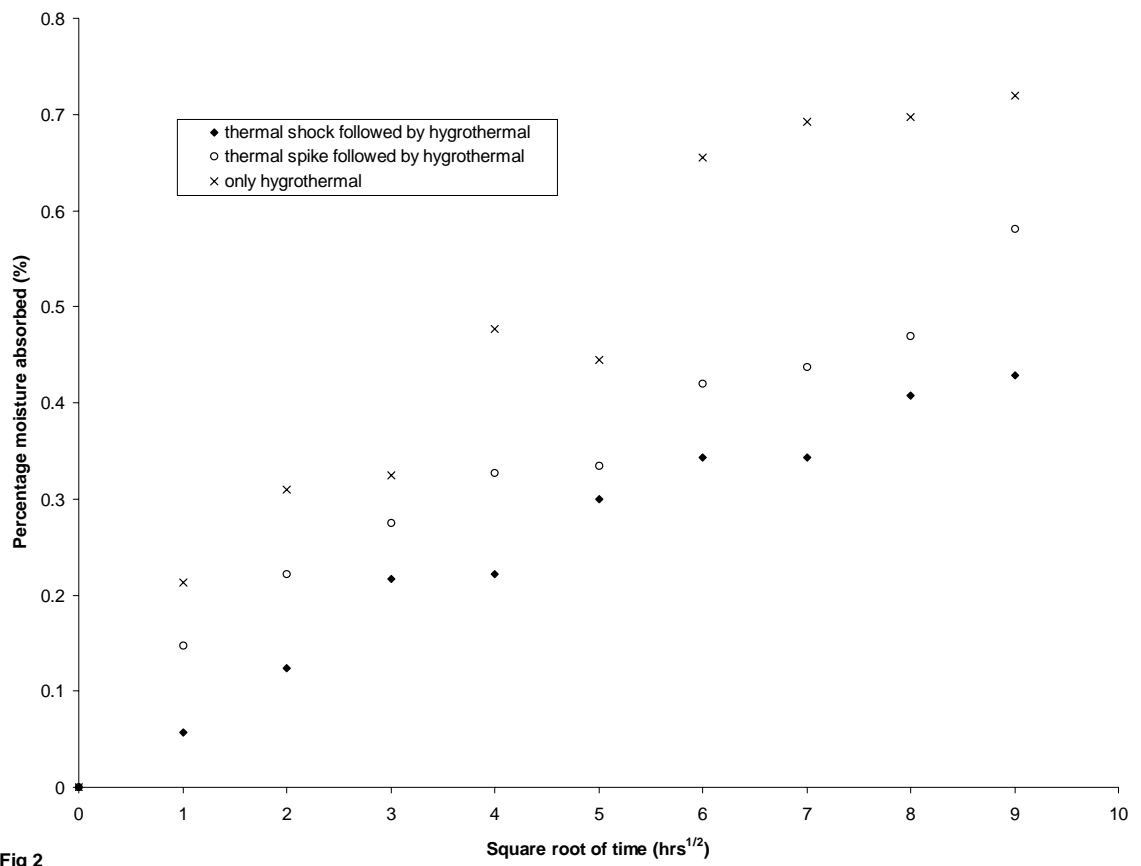


Fig 2

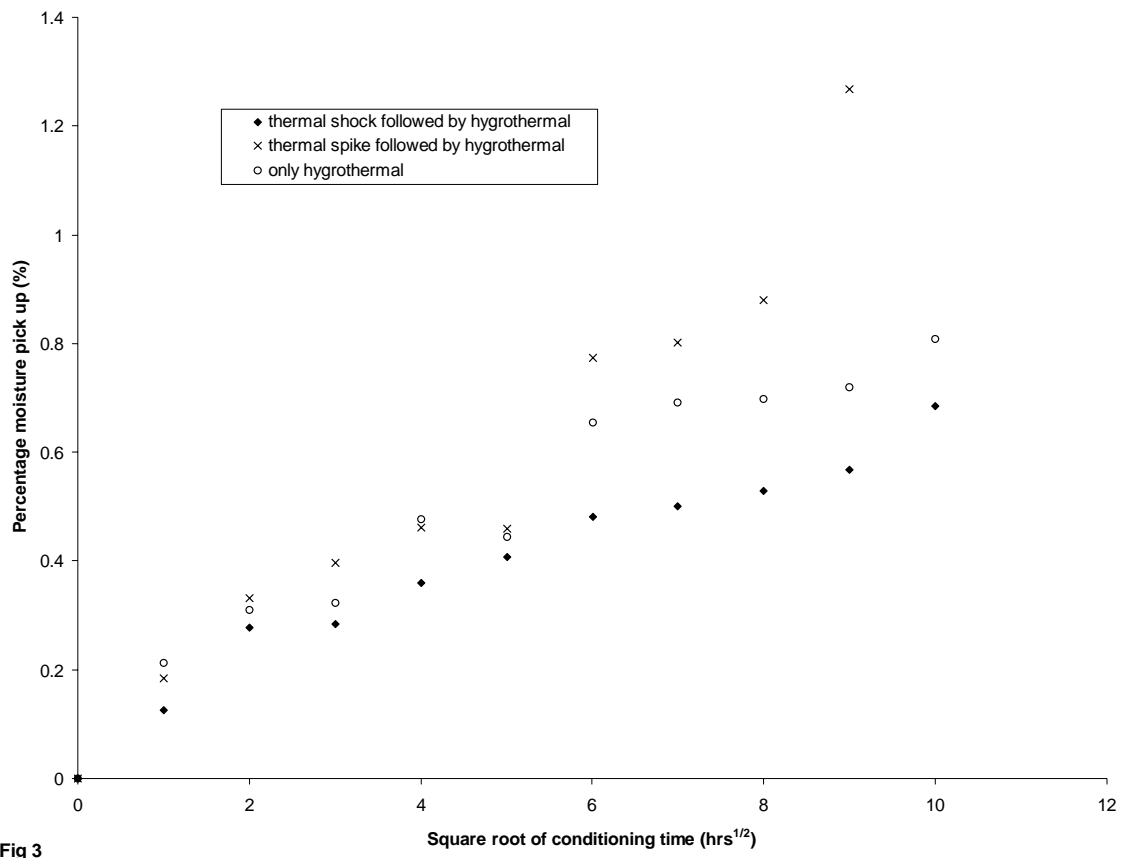


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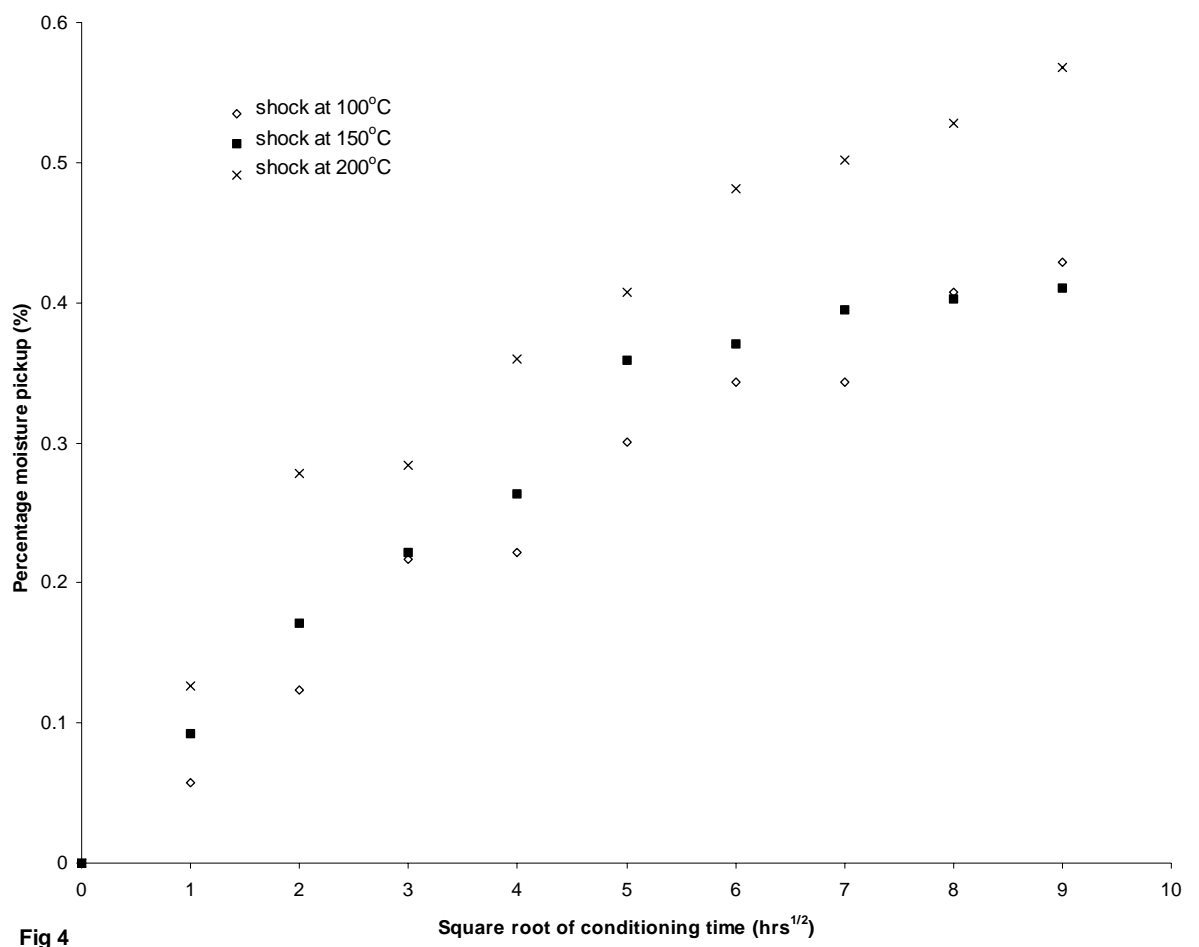


Fig 4

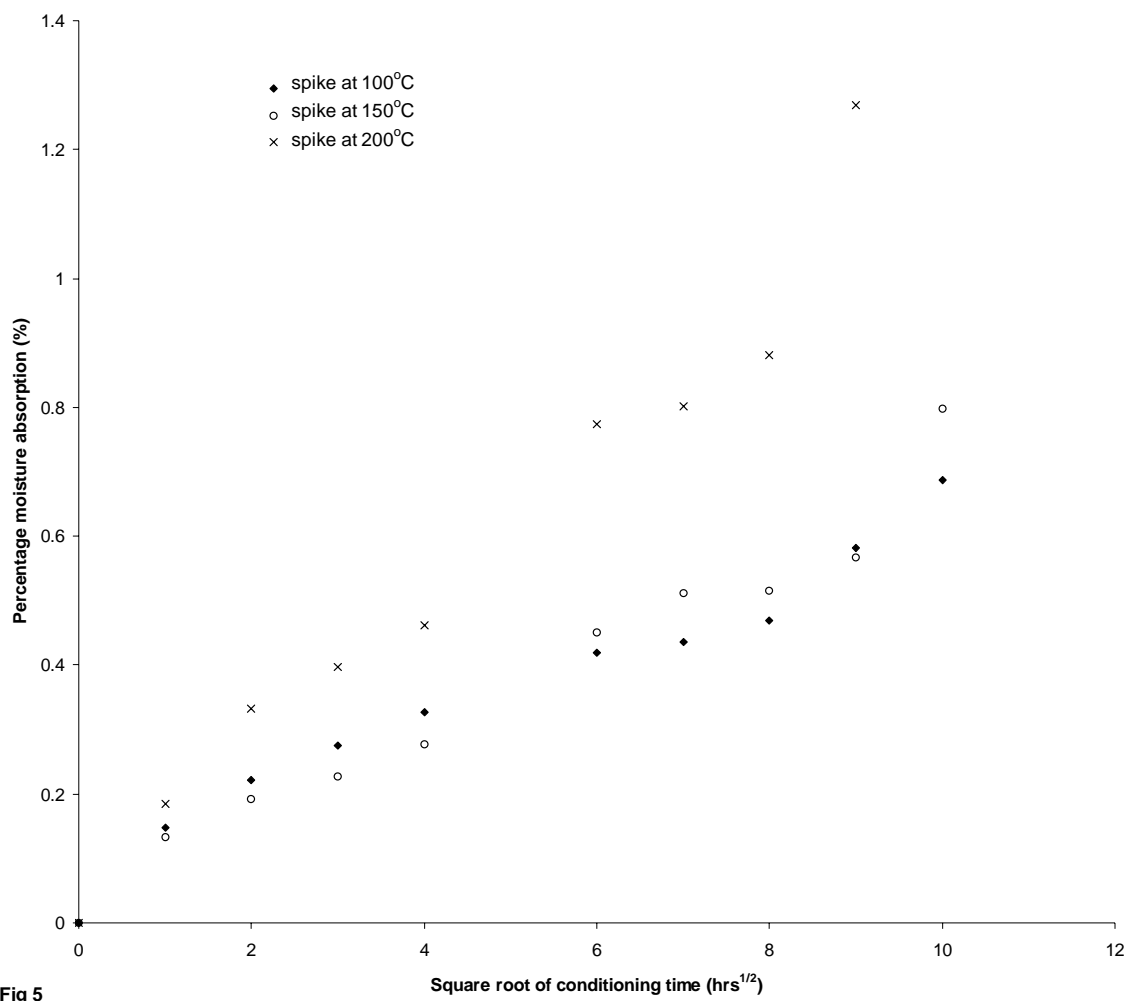


Fig 5

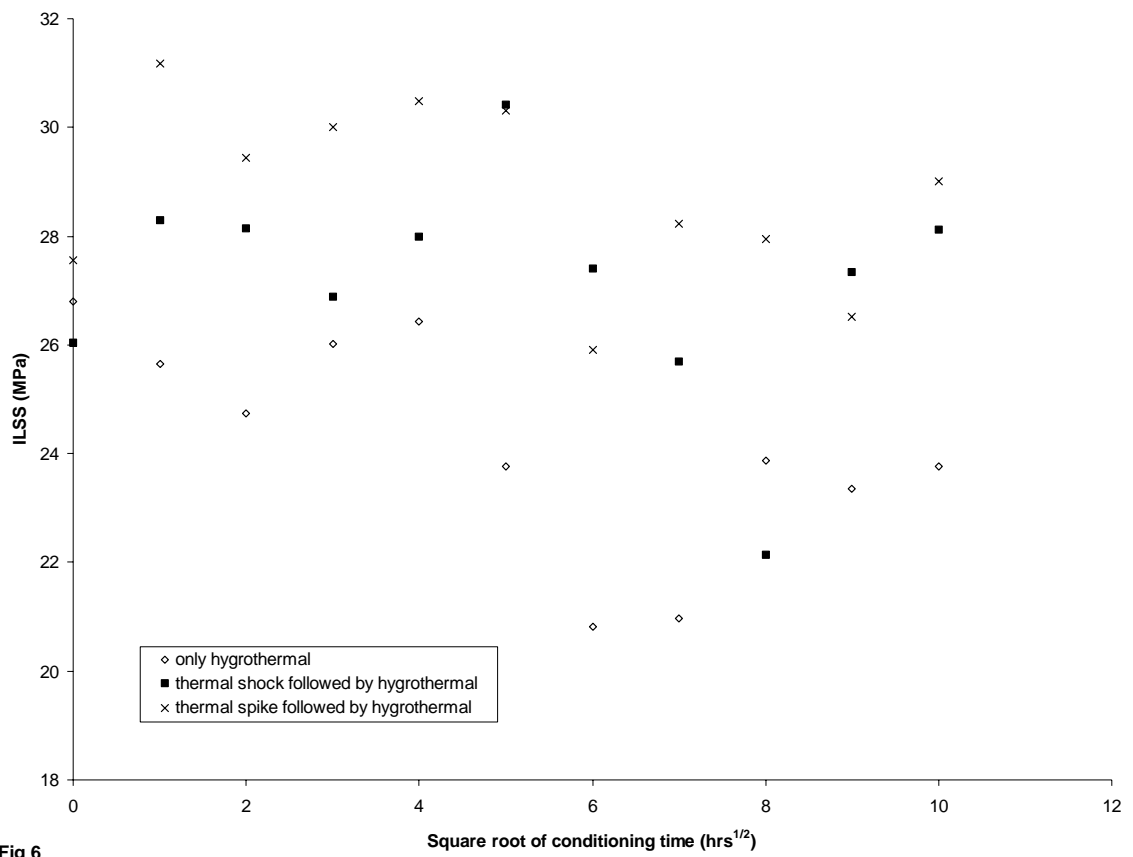


Fig 6

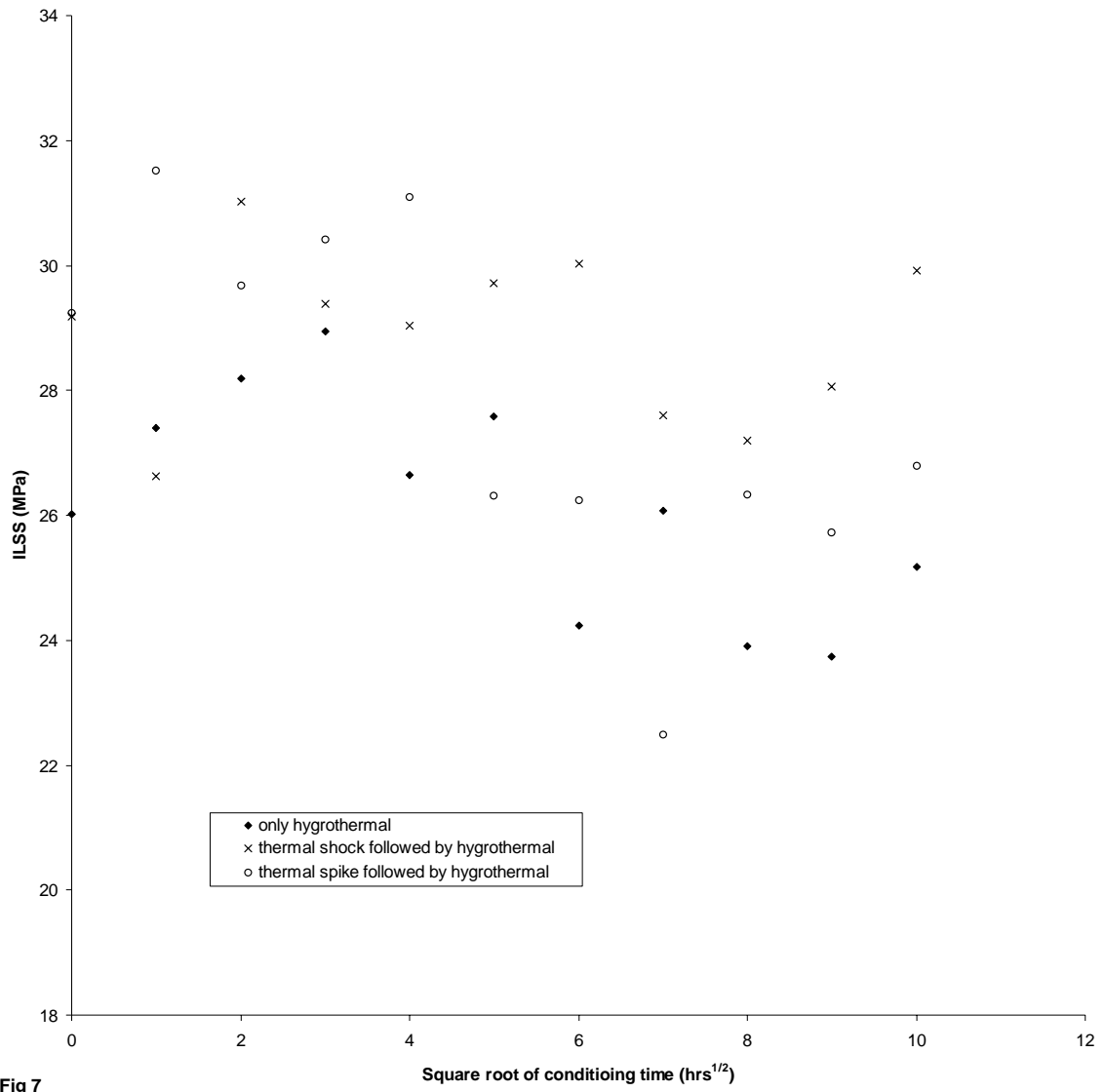
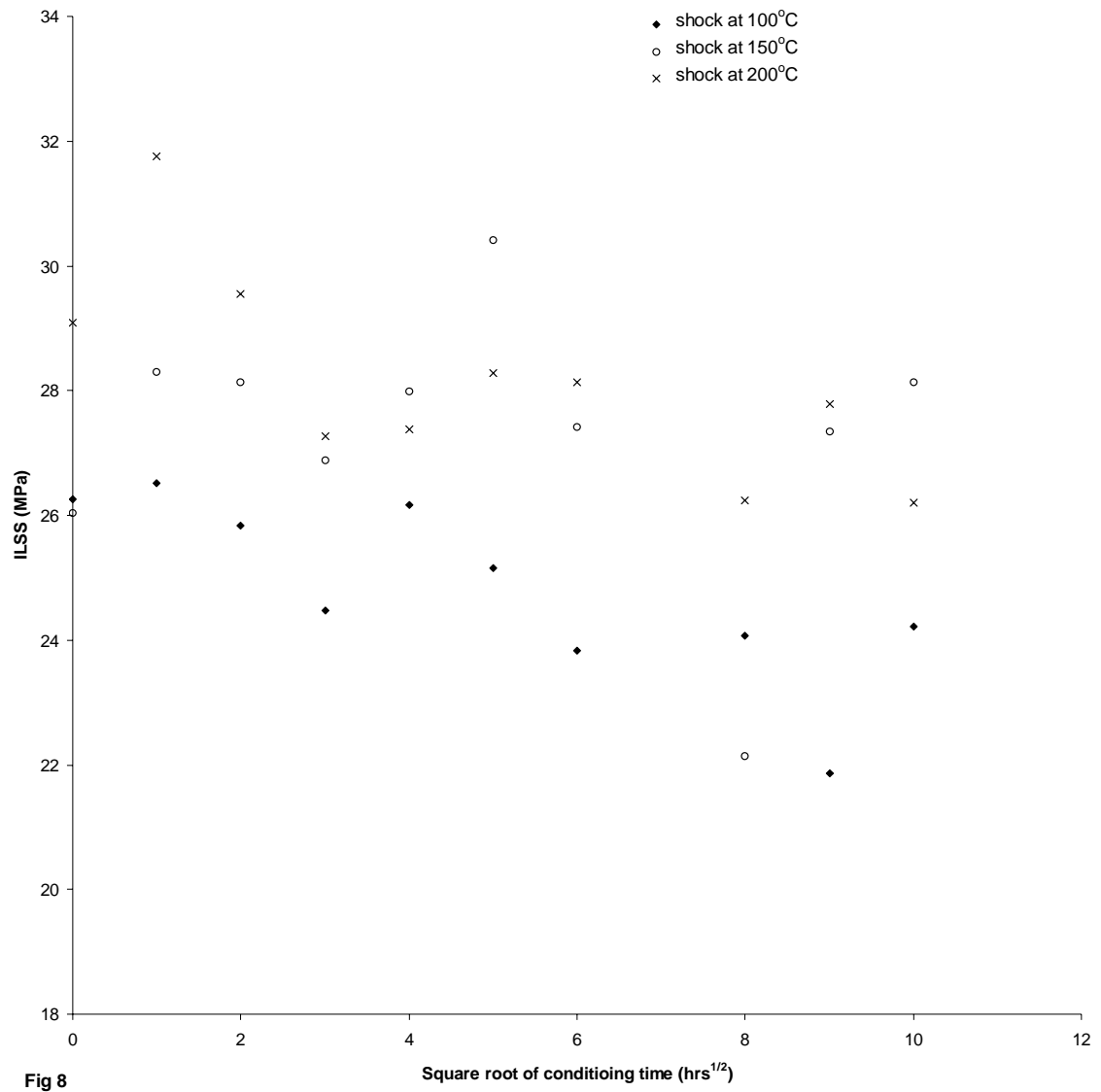


Fig 7



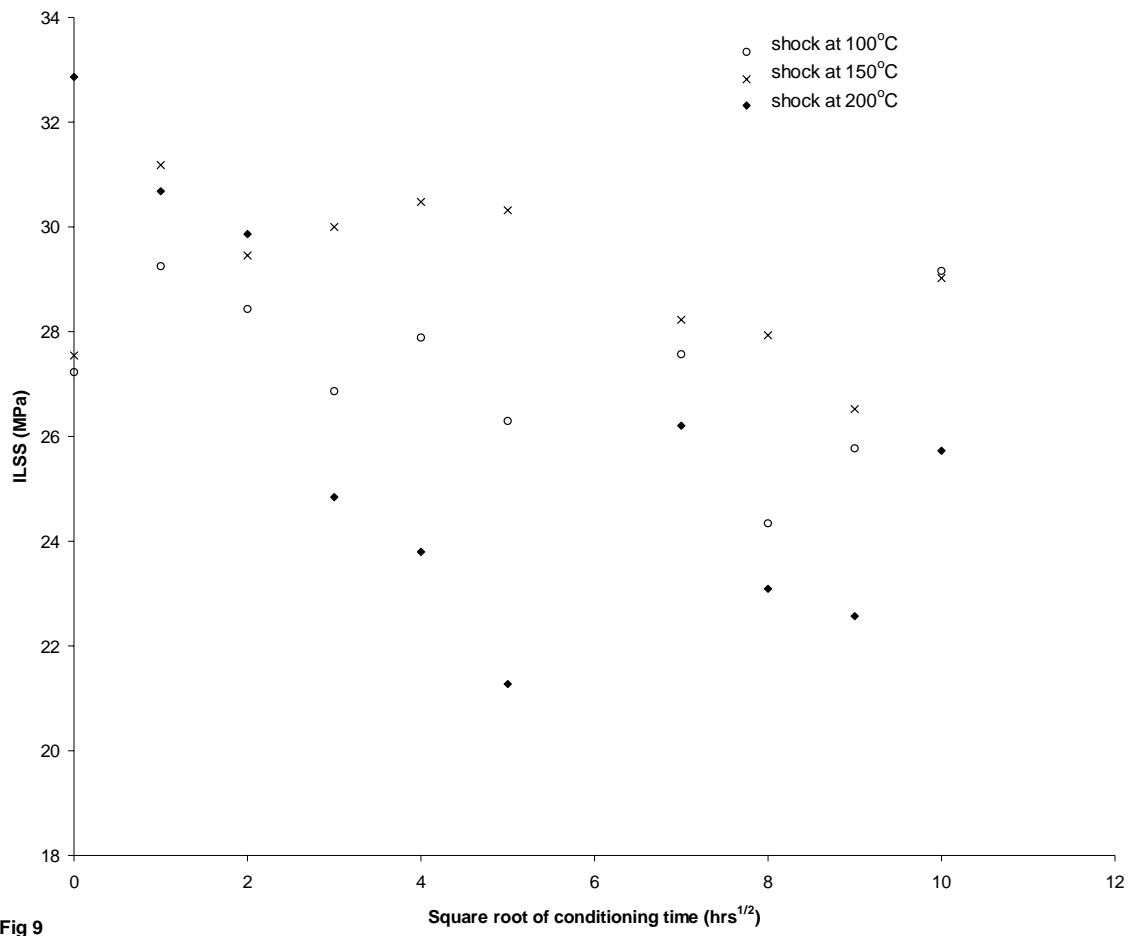


Fig 9

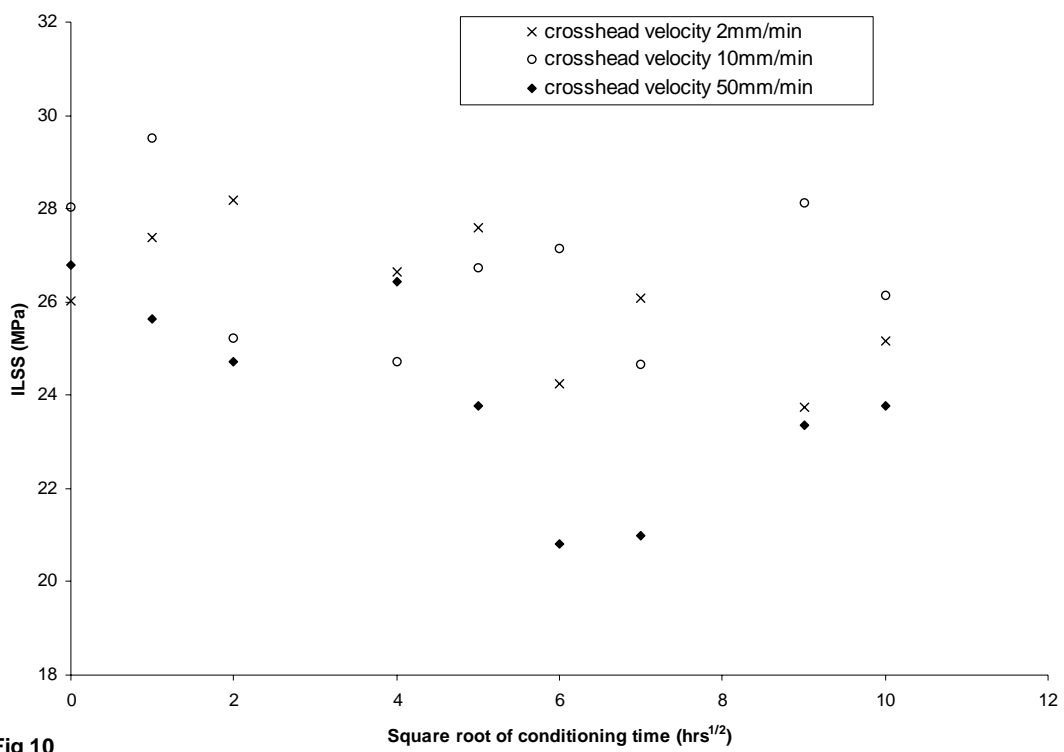


Fig 10

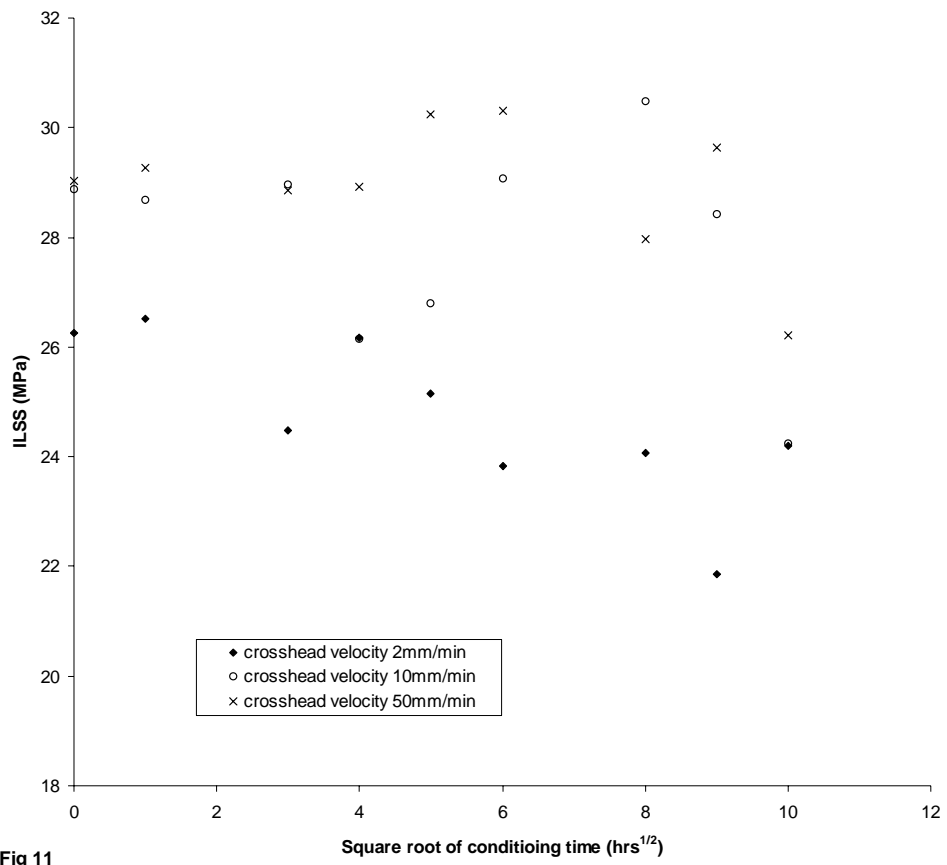
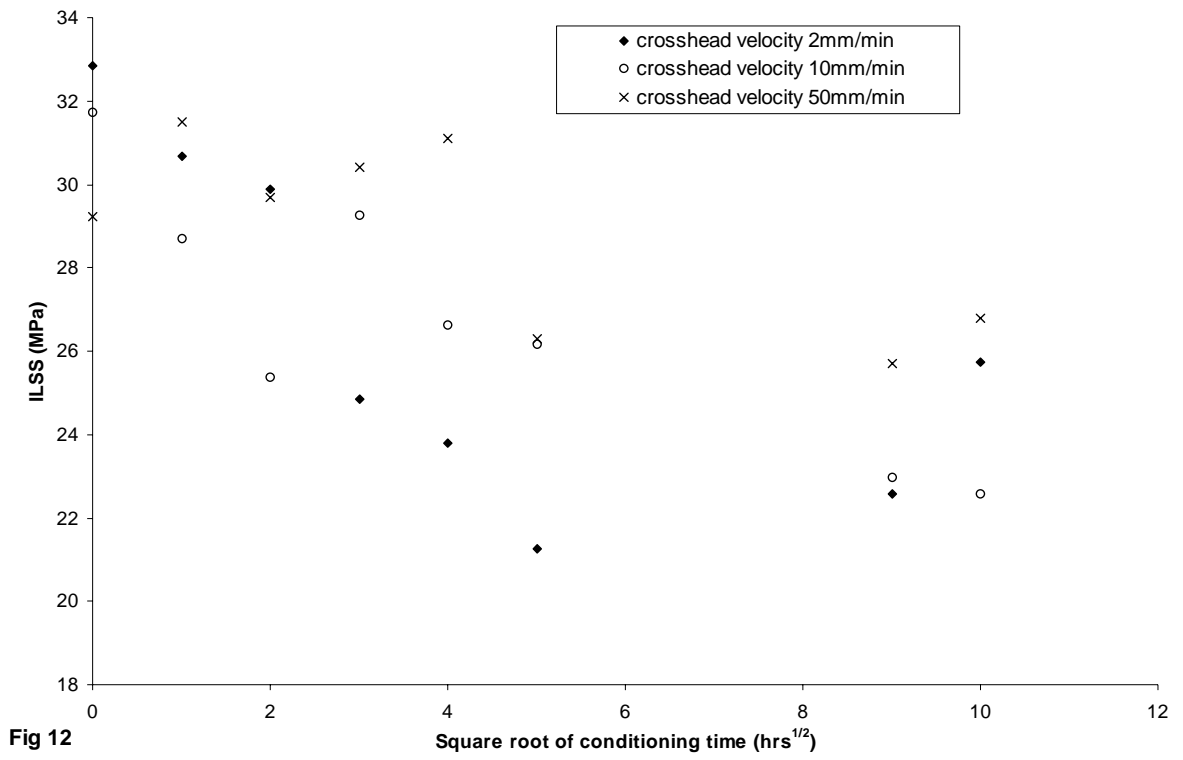


Fig 11



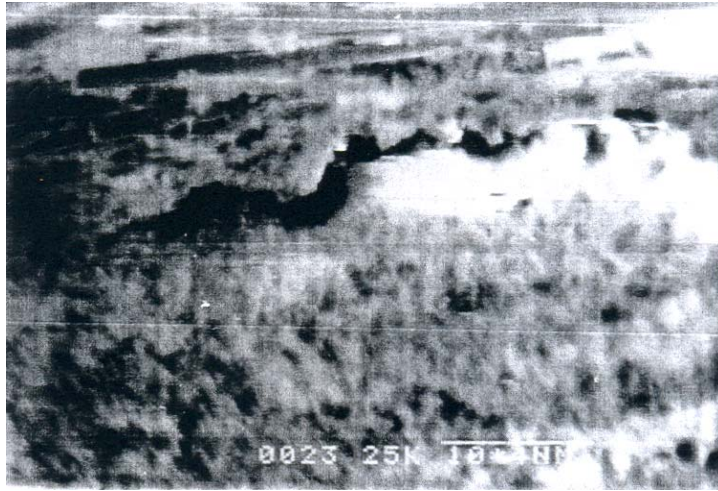


Fig13

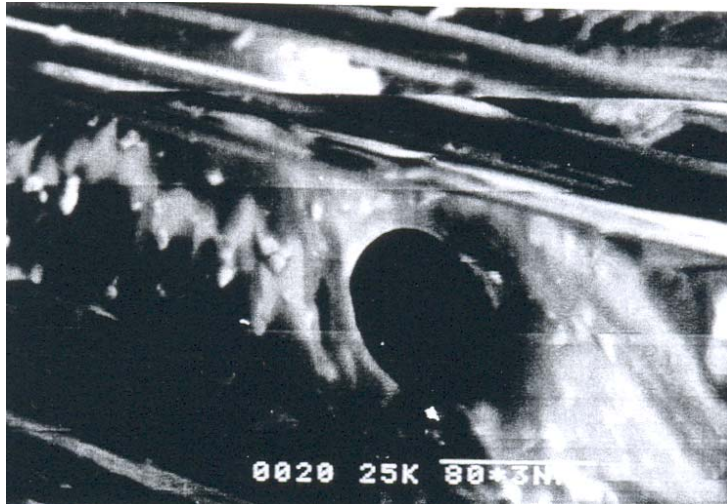


Fig14

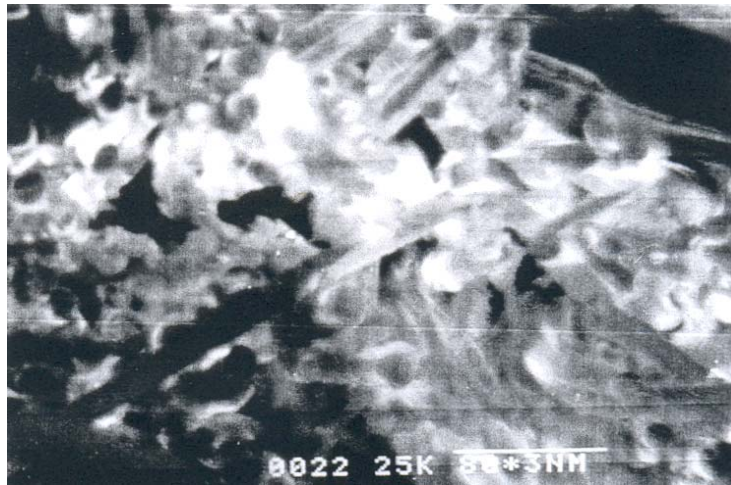


Fig15

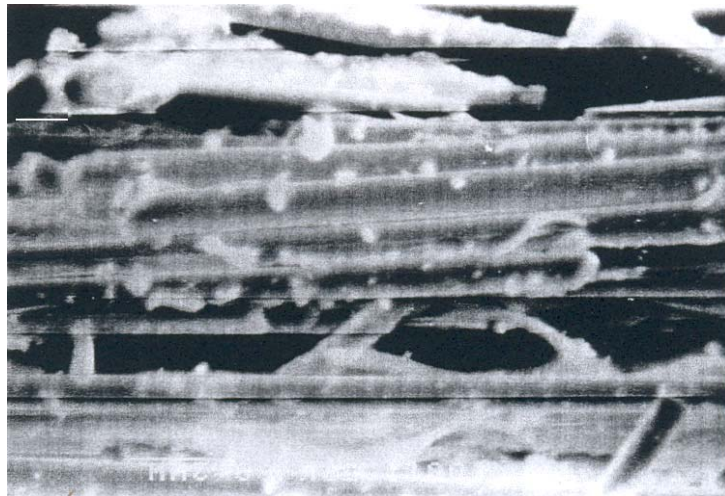


Fig16