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# Effects of Hydrothermal Aging on Mechanical Behavior of Sub-zero Weathered GFRP Composites

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## ABSTRACT

Sub-zero weathered GFRP (glass fiber reinforced plastics) composites were aged in water at 60$^{o}$C for different conditioning times to study fluid sorption kinetics under the influence of a thermal gradient. The effect of subsequent freezing of the conditioned samples on the retention of prior thermal history has been investigated. The variation in mechanical properties during the aging process was studied. One batch of the hydrothermally conditioned specimens was further subjected to sub-zero treatment at –20$^{o}$C temperature. The samples which were subsequently frozen showed higher interlaminar shear strength (ILSS) initially, although this trend was reversed after a certain conditioning period. Thus, the present study aims to evaluate the mechanical behavior of polymer composites under the influence of extreme and complex conditions.

**KEY WORDS**: composite materials, diffusion, mechanical properties, polymer, sub-zero temperature, thermal gradient

## INTRODUCTION

Fiber reinforced polymer (FRP) composites are nowadays widely used in aerospace and electronic applications and sports industries due to their high specific strength, corrosion resistance and inherent vibration damping properties [1,2]. The components during service life in aircrafts are subjected to kinetic heating in humid conditions [2,3]. In wet or humid conditions these materials absorb water. The absorption of water results in swelling stresses within the matrix. These stresses may initially counteract the curing stress thereby resulting in an initial increase in the ILSS [1,3,4]. Long-term exposure to elevated temperature also enhances cross-linking by post-curing mechanisms. This increases the laminate's stiffness thereby reducing the fracture toughness. The effects of long-term exposure in high humidity environments however are more damaging [4]. We observed that with the increase in absorption of water in hot and wet conditions by the FRP composites, the mechanical properties generally deteriorate [5,6].

The present work aims to study the effect of a thermal gradient on the water absorption kinetics. The thermal gradient is set up by exposing the composites to sub-zero temperatures and then exposing them to a beaker of water at an elevated temperature. After the hydrothermal treatment of the specimens, one batch was subjected to sub-zero temperature again. This results in freezing of the water inside the composite specimens. The basic objective of freezing the hydrothermally conditioned specimens was to check whether the thermal history was retained after hydrothermal conditioning followed by subsequent freezing. A comparative study has thus been made with respect to the effect of frozen water and plain water on the interlaminar shear strength (ILSS) of the FRP specimens.

## EXPERIMENTAL

### Materials

E-glass fiber woven cloth (Saint Gobain) of density of 0.36 kg/m$^2$, epoxy adhesive (Ciba-Geigy LY-556 Araldite, HY-951 hardener 10% by weight of epoxy) and polyester with 1% accelerator and 1.5% catalyst with a starting fiber matrix ratio of 60:40 were used to fabricate the composite laminates.

### Preparation of Samples

The GFRP composites were fabricated by hand lay-up method. First, the glass fibers were cut to required dimensions and placed on the plane mould. Catalyzed epoxy was then applied on it uniformly and another layer of fiber was put on it. Rolling was carried out with uniform pressure in order to remove the air pockets. Similarly glass fiber – polyester laminates were also prepared.

After curing samples were cut to required dimensions for three-point bend test as per the ASTM standard D2344-84. Samples were properly dried by keeping in a dessicator for 100 hours. The samples were then marked for subsequent studies. Their initial weights were taken for subsequent water gain studies. The data series in all figures represent the mean of multiple tests.

### Hydrothermal Treatment of Samples and 3-Point Short Beam Shear Test

All the batches of samples were transferred to a freezer maintained at –20$^o$C and kept there for one hour so as to (i) to homogenize the temperature through out the sample and (ii) to give an initial thermal shock to accelerate the water pickup rate by setting up a steep thermal gradient during hydrothermal conditioning. Then they were transferred to a hot water beaker maintained at 60$^o$C for hydrothermal treatment. The different batches of samples were conditioned for different length of times starting from an initial time t = 0 hours to t = 64 hours. Each batch of samples was further subdivided into two sets. One batch of samples after certain period of conditioning were analyzed for water gain and then tested to ascertain their

ILSS. The other set of hydrothermally conditioned samples were again transferred to freezer maintained at –20$^{o}$C for a period of one hour. The ILSS values of these samples were also evaluated and compared with those of the hydrothermally conditioned samples (sans freezing). The three-point short beam shear bend tests were carried out at a crosshead velocity of 2 mm/min, at ambient temperature of 31$^{o}$C. The span length of the specimen was 34 mm. The shear strength was calculated by using the following formula

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

Where $P_b$ = breaking load

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

## RESULTS AND DISCUSSION

Figures 1 and 2 show the plots of ILSS and percentage water gain versus conditioning time for polyester and epoxy matrix composites respectively. These plots indicate that with increased conditioning time, water absorption increases gradually up to a certain level; at higher conditioning times the water pickup becomes almost constant. The ILSS increases initially, followed by a gradual decrease to lower values for glass-polyester composites [Fig. 1]. However, the epoxy matrix composites show a continuous decrease in the values through out the entire conditioning period [Fig. 2]. Clearly water absorption is a function of time [7]. The water uptake is also enhanced by the presence of a thermal gradient [8]. The initial thermal gradient acts as an active accelerator for increased water uptake in the initial period [9]. At the higher exposure time, water absorption became almost constant. This may be due to the fact that maximum amount of water absorption by composites is a function of thermodynamic potentials of water and the composite [3,10]. With progressive water absorption during the initial period the potentials of the surrounding water and the composite tend to equalize, thereby resulting to a saturation level at higher exposure times.

The initial increase in the ILSS in glass-polyester composites may be due to post-curing mechanisms, especially at lower conditioning times. Thereafter, a steady decrease is observed in the ILSS. The presence of an active thermal gradient and differential thermal expansion coefficients of fiber and matrix in the glass-epoxy composites could have led to colossal interfacial damage which could well outweigh the beneficial post-curing effects. That may be the reason in decrease in ILSS for the epoxy matrix composites from the very beginning of the conditioning period. The development of increasing swelling stresses with increase in the conditioning time could outweigh the advantageous effect obtained during the initial post-curing. Cracks act as fast diffusion paths for fluid transport in the polymeric matrix. So, once a crack develops at the matrix or at the fiber-matrix interface or interphase, water absorption occurs very rapidly, which further enhance the debonding mechanisms along with other damaging phenomena. This leads to a fall in ILSS values, as reflected in figures 1 and 2.

The ILSS for subsequently frozen polyester composites increase when compared with the ILSS of hydrothermally conditioned specimens up to a certain period of time after which a decrease is observed. This is shown in figure3. During curing, shrinkage occurs which resulting in development of shrinkage stresses. Once the composite is exposed to hot and humid conditions, fluid pickup starts and swelling stresses of opposite nature are developed. As the water is frozen, anamolous expansion occurs, causing further stressing of the material. The interplay of these stresses result in mutual nullification [11, 12]. Thus temporarily, the composite becomes stress-free, and this is reflected in an increase in ILSS in this period. Freezing stresses are absent in the hydrothermally conditioned specimen which were not subsequently frozen. Consequently, the initial strengthening is not as prominent. At higher conditioning times, just the reverse phenomenon takes place; more amount of water is added and thus swelling stresses and the stresses developed due to freezing of water is more than the compressive stresses developed due to the shrinkage of composites. Because of the presence

of a resultant tensile stress, development of microvoids and other defects such as swelling and fiber debonding may happen. Hence, deterioration of the material occurs thereby leading to the lowering of ILSS. At higher conditioning the effect of subsequent freezing has a more deleterious effect for the same water content as compared to the specimens which are not subsequently frozen.

Figure 4 shows a gradual fall in ILSS with exposure time for both hydrothermally conditioned specimens as well as those specimens that were frozen following hydrothermal conditioning for glass-epoxy composites. The shear strength for hydrothermally conditioned and subsequently frozen specimens shows slightly higher value as compared to the specimens that were not subsequently frozen up to a certain length of conditioning period, although there is a gradual fall in ILSS for both with increasing conditioning time. The gradual fall in ILSS value could be due to progressive damage in the matrix and fiber-matrix interface. The improvement in the shear strength for frozen specimen may be due to the nullification of various stresses developed inside it. Epoxy resins have lower shrinkage on curing and a lower coefficient of thermal expansion. These resins are also characterized by their good adhesiveness with glass fibers [13]. Hence, unlike glass-polyester composites, the effect of frozen water is statistically less significant in glass-epoxy system. That could be attributed by better adhesion chemistry at the fiber/epoxy interface.

Figures 5 and 6 show the scanning electron micrographs of the composite samples after environmental conditioning. Figure 5 shows the scanning micrograph of a glass-polyester specimen after two hours of conditioning. The matrix damage is clearly evident in the form of a central matrix crack and a slight coagulated polymer outcrop. A considerable damage is also visible in the form of de-adhesion of fibers. Figure 6 shows a similar micrograph for epoxy composites. The upper portion of the scanning electron micrograph gives a good account of the lack of explicit damage and matrix cracks. This may be attributed to better bonding properties of the epoxy resin [13].

Water 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 [7]. The water distribution inside the material never attains a steady state. It changes continuously, the water concentration depending on time and position [10].

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 [14]. Shear failure in the interphase could be caused by interfacial shear failure between the fiber and interphase itself [15]. 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 effect of a thermal gradient on the water absorption kinetics and mechanical behavior of glass-epoxy and glass-polyester composites have been assessed here. It appears that there is an increase in the values of ILSS for polyester matrix composites in the initial conditioning period. With increase in exposure time, however, this trend is reversed and the ILSS falls to lower values. But the values of ILSS decrease for epoxy matrix composites through out the conditioning period. The extent of the initial rise and subsequent fall in the ILSS values appear to be a function of the state of water (plain/frozen) present inside the specimens. The presence of frozen water results in a greater initial increase in the values of ILSS, but with prolonged exposure a deleterious effect is observed. The effect of further freezing is seen to be statistically less significant in the glass-epoxy system, possibly resulting from the better interfacial bonding strength. It may also be stated that the environmental sensitivity is a more dominant factor in the glass-polyester system as compared to the glass-epoxy system.

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## Figure Captions

**Figure 1** A comparison of water absorption and ILSS with increasing exposure times for glass-polyester composites

**Figure 2** A comparison of water absorption and ILSS with increasing exposure times for glass-epoxy composites

**Figure 3** Effect of further freezing on the ILSS of glass-polyester composites

**Figure 4** Effect of further freezing on the ILSS of glass-epoxy composites

**Figure 5** Scanning electron micrograph of glass-polyester composites after 2 hours of conditioning at a magnification of 300X

**Figure 6** Scanning electron micrograph of glass-epoxy composites after two hours of conditioning at a magnification of 250X

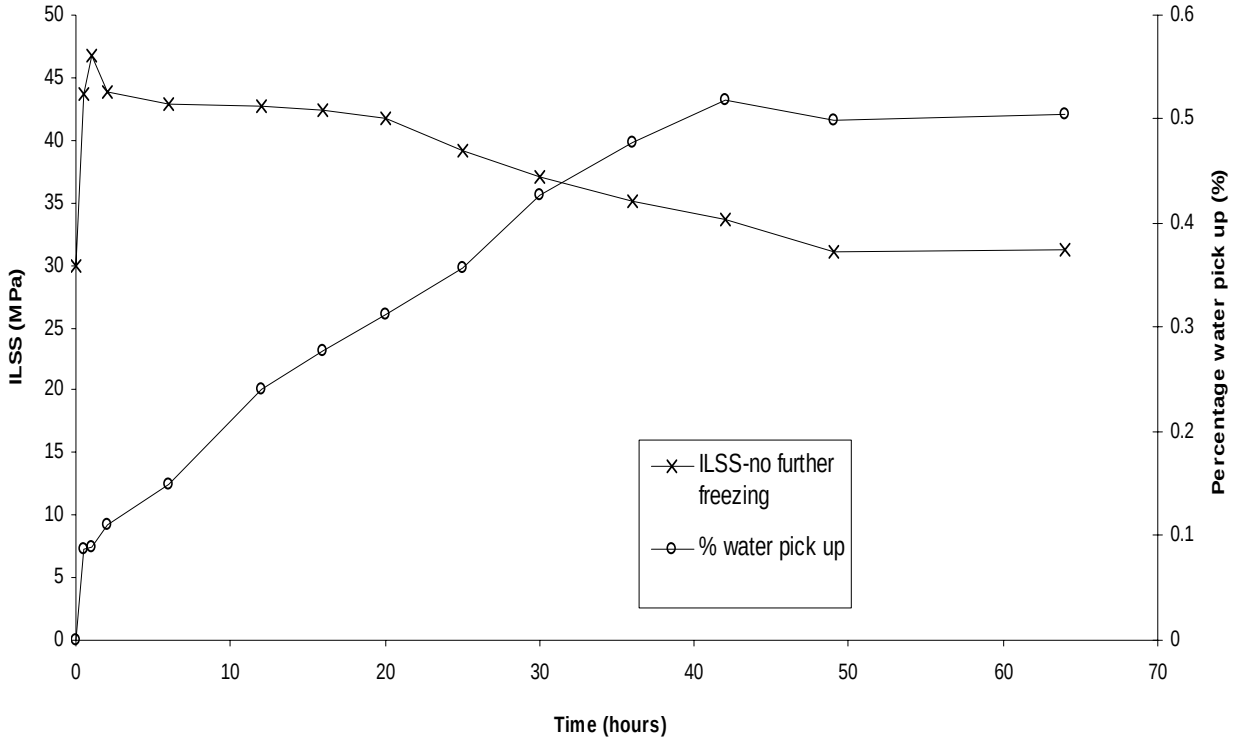
ILSS (MPa)
Percentage water pick up (%)
Time (hours)
ILSS-no further freezing
% water pick up
0
5
10
15
20
25
30
35
40
45
50
0
0.1
0.2
0.3
0.4
0.5
0.6
0
10
20
30
40
50
60
70

**Figure 1**

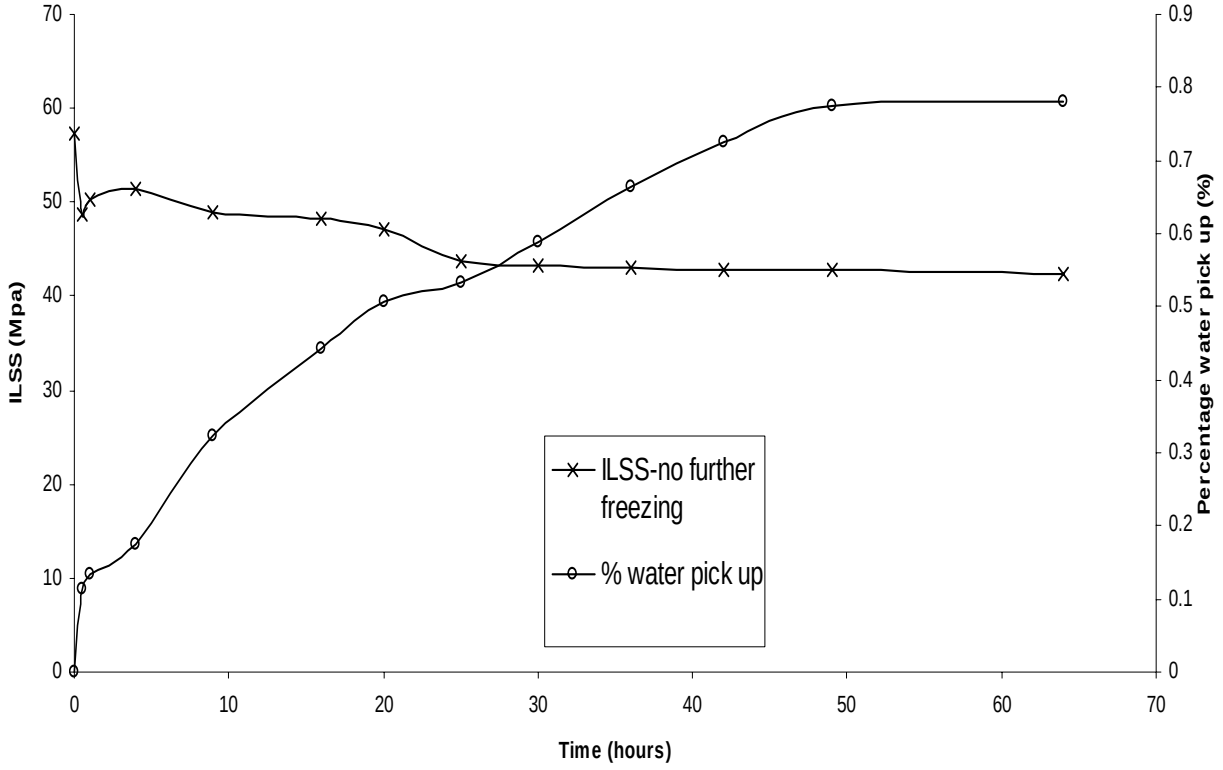
ILSS (Mpa)
Percentage water pick up (%)
Time (hours)
ILSS-no further freezing
% water pick up
0
10
20
30
40
50
60
70
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

**Figure 2**

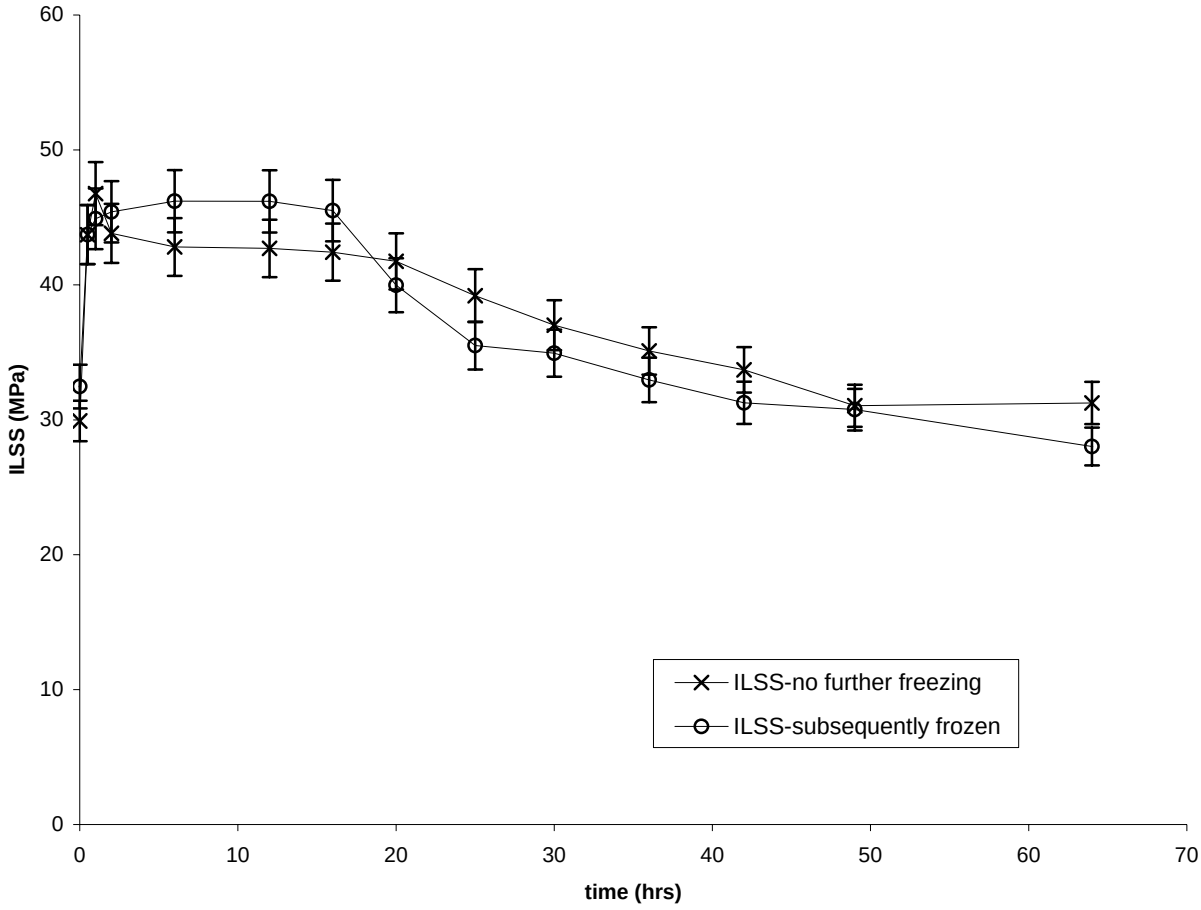
60
50
40
30
20
10
0
ILSS (MPa)
0
10
20
30
40
50
60
70
time (hrs)
ILSS-no further freezing
ILSS-subsequently frozen

**Figure 3**

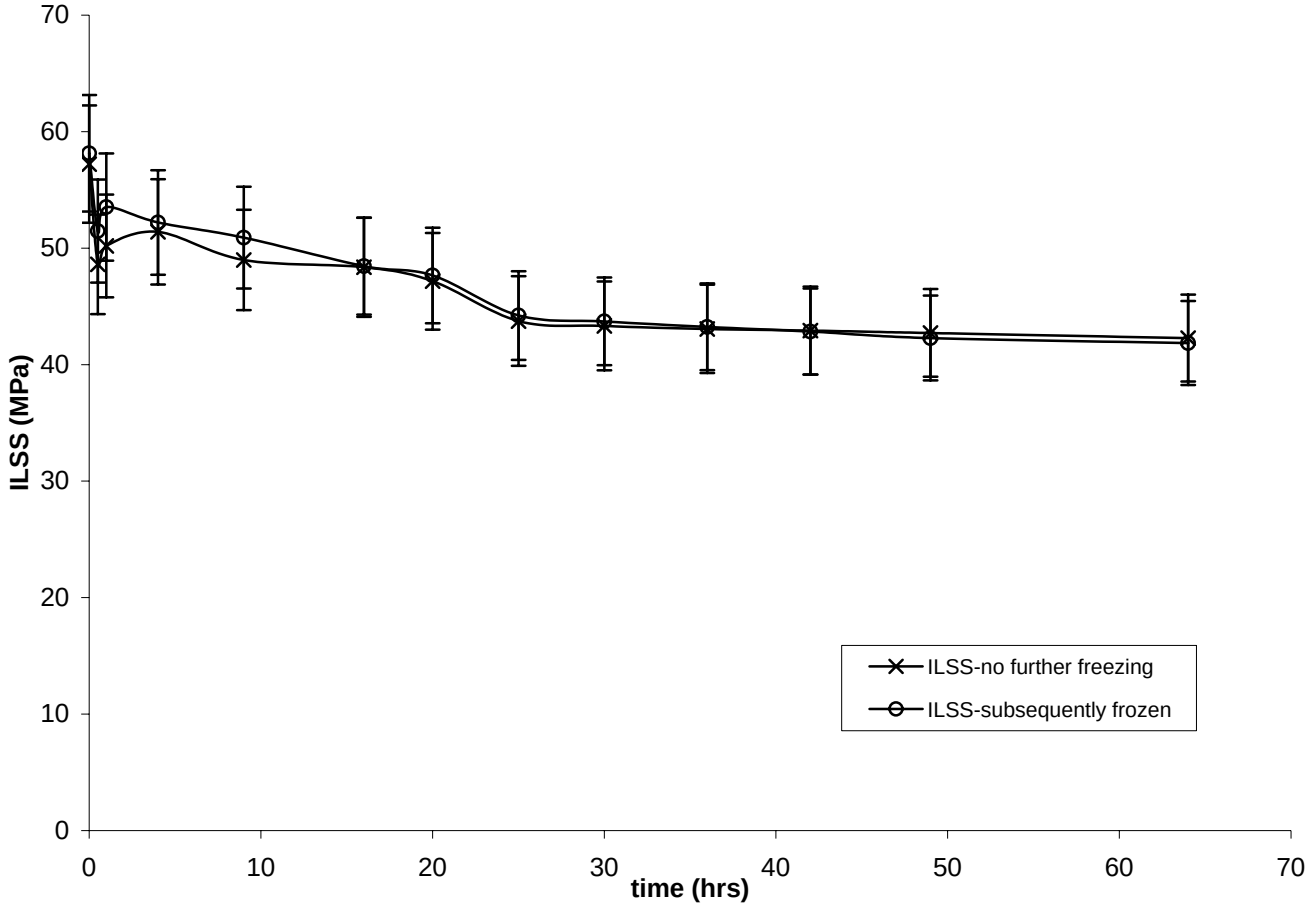
70
60
50
40
30
20
10
0
ILSS (MPa)
0
10
20
30
40
50
60
70
time (hrs)
ILSS-no further freezing
ILSS-subsequently frozen

**Figure 4**

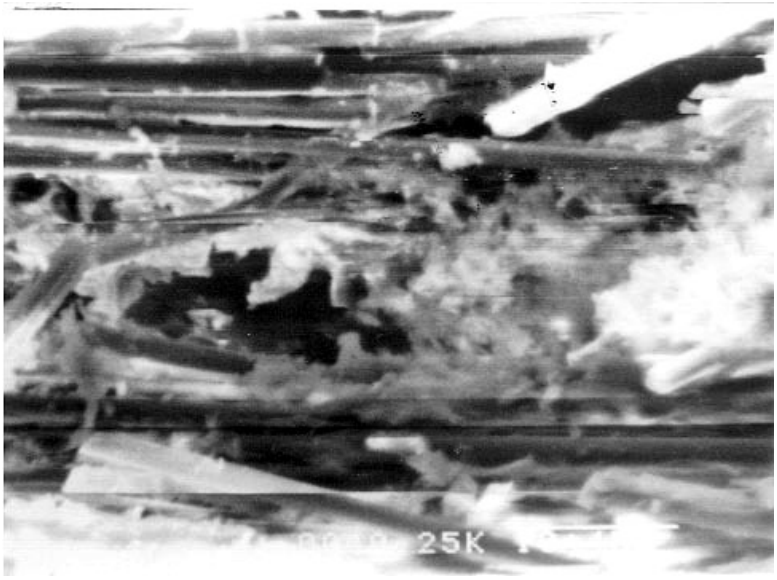


**Figure 5**


**Figure 6**