Mechanical Behavior of Glass/Epoxy Composites at Liquid Nitrogen Temperature

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ABSTRACT

The present experimental investigation deals with the mechanical behaviour of glass/epoxy composites at cryogenic temperature. Woven and chopped E-glass fibres of 50 weight percentage were reinforced with epoxy matrix to prepare the laminated composites. 3-point bend tests were carried out to assess interlaminar fracture behaviour at cryogenic and at ambient conditions. The specimens were tested at a range of 2 mm/min to 500 mm/min crosshead speed to evaluate the sensitivity of mechanical response during loading at these conditions. The mechanical performances of the laminated specimens at cryogenic conditions were compared with room temperature property by using SEM photographs. DSC was carried out to study whether there is any change in glass transition temperature. Glass/epoxy composites were found to be loading rate sensitive. DSC analysis shows increase in glass transition temperature after cryogenic conditioning which may be due to irreversibility of the chain mobility. Phenomenological behaviour of these composite materials may be attributed by polymer relaxation at low temperature, cryogenic hardening, matrix cracking, and misfit strain due to differential thermal coefficient of the fibre and the matrix and also by enhanced mechanical keying factor by compressive residual stresses generated at cryogenic temperatures.

Keywords: Epoxy, Composites, Liquid Nitrogen, Mechanical Properties, Thermal Expansion, Superconducting Magnets

INTRODUCTION

In recent years characterization and mechanical behaviour of polymer composites at cryogenic temperature has been focused. These are the modern engineering materials that have wide applications in a range of areas from aerospace, automobiles and boats to cryogenic equipments such as cryogenic fuel tanks, cryogenic fuel delivery lines, cryogenic wind tunnels and parts of the cryogenic side of turbo-pumps because of their ease of handling, low fabrication cost and excellent mechanical properties. Epoxy resins as the matrix for fibre reinforced plastics have been used in cryogenic tankage in RLV (Reusable Launch Vehicle) thermal insulation, electrical insulation, structural support and adhesives for vacuum tight joints [1], as well as in permeability barriers, which provide minimal structural support in superconducting magnets at low temperatures [2]. When the temperature is decreased down to cryogenic temperature internal stresses are generated in the epoxy matrix due to thermal contraction. Fracture of the matrix is induced when the thermal stress induced stress intensity factor exceeds the fracture toughness of the resin. The fracture toughness of the matrix at cryogenic temperature can be improved by controlling the chemical structure, network structure and morphology [3]. The microstructure becomes more orderly at low temperature [4].

In fibre reinforced plastics residual stresses are generated due to difference in CTEs (Coefficient of Thermal Expansion) between the matrix and the reinforcement which are relieved by physical process such as potholing, debonding at matrix/fibre interface, microcrackings etc. when they become large enough. The amount or density of microcrackings depends mainly on the tensile modulus of fibres and the matrix properties used in the composite. Addition of toughening agents in the matrix decreases the microcracking propensity of these laminates [5]. Complex stress patterns and numerous stress raisers arise in the matrix from a thermal mismatch with the glass fibres resulting in a variable and unpredictable failure pattern [6]. Residual stresses can be minimized by choosing the optimum ply angle [7] or by altering CTE of the matrix chemically to closer match the CTE of fibres. Some experiments reported improved mechanical properties of glass/epoxy laminates at low temperature [8]. Glass fibres and epoxy resins are known to be highly loading rate sensitive. The mechanical properties of glass reinforced epoxy composites are found to be rate sensitive even at low strain rates [9].

To study the loading rate sensitivity of polymeric composites at low temperature is of prime importance. CFRP structural components used in aircrafts can suffer high and low velocity impact at cryogenic temperature. Fibre reinforcement architecture and stacking sequence play an essential role in the behaviour of composites under such thermal and loading conditions [10]. In this work, the mechanical behaviour of chopped glass/epoxy composites were compared at cryogenic and at room temperature. DSC test was carried out to study whether there is any change in glass transition temperature after cryogenic treatment.

EXPERIMENTAL

Material

Araldite LY-556, an unmodified epoxy resin based on Bisphenol-A and hardener (Ciba-Geigy, India) HY-951, aliphatic primary amine were used with chopped E-glass fibers treated with silane based sizing system (Saint-Gobain Vetrotex) to fabricate the laminated composites.

Fabrication of Composites

The chopped glass fiber/epoxy composite laminates were fabricated by wet lay-up method; the chopped glass fiber cloth of required dimension was laid over a mould and then catalyzed epoxy resin was poured absorbed over the reinforcement. The wet composite was rolled, to distribute the resin and to remove the air pockets. The sequence was repeated until the desired thickness was obtained. The layered structure was allowed to harden on cure. It was cured at room temperature for 48 hours. After curing, the laminate was cut into the required size for 3-point bend (Short-Beam Shear) test by diamond cutter. Then stability test was done for the composite laminates. Here the laminates were weighed and then heated in an oven at 50 oC. The weight is intermittently checked till we get a stable weight, that is, with further heating there is no change in the weight of the composite.

Cryogenic Conditioning

After the stability test the samples were allowed to come back to the ambient temperature. Then they were kept in the desiccators so that there is no further absorption of moisture. The samples to be cryogenically treated were exposed to liquid nitrogen environment (77K) for one hour. After the exposure one batch of samples were taken out and kept at room temperature for one hour. Another batch of samples was tested in 3-point bend test immediately after exposure to cryogenic temperature.

Short Beam Shear Test

The 3-point bend tests were carried out for first batch of samples immediately after exposure to cryogenic temperature. The former samples after exposure to room temperature and the untreated as-cured samples were tested in 3-point bend test at room temperature. All the mechanical flexural tests were performed at 2, 50, 100, 200 and 500 mm/min crosshead speeds. Then breaking load and strain at maximum load was measured from stress vs strain graphs for all the samples.

DSC Analysis

The DSC measurements were performed on a Mettler-Toledo 821 with intra cooler, using the STAR software with Alternating DSC (ADSC) module. The temperature calibration and the determination of the time constant of the instrument were performed by standards of In and Zn, and the heat flow calibration by In. The underlying heating rate of $10^{o}Cmin^{-1}$ was used. In order to calibrate the heat flow signal, a blank run with an empty pan on the reference side and an empty pan plus a lid at the sample side was performed before the sample measurements. Standard aluminium pans were used. The experiments were performed in the temperature range from $40^{o}C$ to $100^{o}C$.

RESULTS AND DISCUSSION

Figure 1 and figure 2 shows the effect of crosshead speeds on ILSS values at cryogenic temperature, ambient temperature after exposure to cryogenic temperature and at ambient temperature of untreated samples of chopped and woven glass/epoxy laminates. As chopped fibres provides more surface area than woven fibres, the amount of effective bonding with the available polymer matrix per unit surface area of the fibres will be less results in lower ILSS values than woven fibre composites. From figure 1 and figure 2 we note that the nature of the curve is different at above and below 50 mm/min crosshead speed. The ILSS value increases initially and decreases thereafter. The cryogenically conditioned laminates showed higher values than untreated laminates for both chopped and woven glass/epoxy composites. At lower strain rate the epoxy matrix is more ductile than the composite which may contribute to lower ILSS values at lower crosshead speed. The matrix acts as the load transfer medium between the fibres, hence the performance of the composite depends on the capability of the matrix to transfer load through the interface. At lower speed the there will be more deterioration in the matrix as more time is available for failure to take place results in lower ILSS values which increases with the crosshead speed [11]. At higher loading rates the reduction in ILSS values may be due to the restriction and minimization of relaxation process at the crack tip leading to the growth of stress induced cracks without blunting. The matrix is unable to transfer the load properly due to less availability of time at higher speed i.e. the load on the matrix is like an impact. Several damage mechanisms may appear such as fibre fracture, matrix cracking, fibre pull-out and delamination. Hence it can be concluded that the laminate requires an optimum time to transfer load effectively through the interface.

The conditioning at cryogenic temperature may result in cryogenic hardening of the epoxy matrix. There may be generation of microcracks in the matrix due to thermal shock. These can be avoided by slowly decreasing the temperature from room temperature. The ILSS reflects the resistance of a layered composite material to forces that tend to induce a relative motion between the layers parallel to them. Thus, the sign of improvement in the shear value after cryogenic conditioning is probably due to differential thermal contraction (figure 3 and figure 4) of the matrix during sudden cooling which leads to the development of greater cryogenic compressive stresses and may increase the resistance to debonding and better adhesion by mechanical keying factor at the interface between fiber and the matrix [12, 13]. The rise in ILSS value may be attributed to the improved adhesion by cryogenic conditioning and also by the post-curing strengthening phenomena [1]. The cryogenic hardening was found to be one of the prominent factors responsible for enhancement in wear performance of composites [14]. It was observed that more amount of matrix residue adhered (figure 5) to the fibre for cryogenically conditioned specimens. This may be due to increase in friction and adhesion between fibre-matrix depending on the compression by contraction of matrix as the polymer contracts more than the glass.

Failure of the matrix occurs when the stresses greater than the shear strength of the matrix is readily generated. The specimens tested at room temperature after cryogenic conditioning showed lower ILSS values but higher than the untreated specimens. This may be due the relaxation of the compressive stresses generated when cryogenically conditioned.

Figure 6 shows the comparison of glass transition temperature (Tg) of the chopped glass/epoxy laminates of untreated and cryogenically conditioned specimens. There is an increase in Tg after the cryogenic conditioning. Cryogenic conditioning causes freezing of the polymeric molecular chains that restricts motions at low temperature. Here both the motions segmental motion and the total mobility of the molecule as a whole are frozen and the molecular mobility is arrested causing decrease in chain flexibility. The increase in glass transition temperature (Tg) is due to incomplete reversibility of molecular chain mobility. Cryogenic conditioning can be considered as a treatment which makes the microstructure of the composite more orderly. It was reported that damping behaviour of glass/epoxy composites at low temperature is irreversible that is the phase transition because of the temperature change is not always reversible [12]. In case of thermoplastics the degree of crystallinity has increased after the cryogenic treatment which results in marginal increase in glass transition temperature [15].

CONCLUSION

It can be concluded that the ILSS values for chopped fibre composites are found to be lower than woven fibre composites. This can be due to less amount of effective bonding with the available polymer matrix per unit surface area of the fibres. The higher ILSS values for cryogenically conditioned samples is attributed to enhanced mechanical keying factor by the generation of cryogenic compressive stresses which enhances the friction at the interface due to contraction of epoxy matrix at low temperature. The composites laminate needs an optimum time to transfer load effectively through the interface. There is an increase in glass transition temperature after cryogenic conditioning of the laminates which may be due incomplete reversibility of molecular chain mobility resulting in reduced chain flexibility.

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FIGURE CAPTIONS

Figure 1 Variation of ILSS of chopped glass-epoxy composites with crosshead speed at cryogenic temperature (♦), ambient temperature after cryogenic conditioning (■) and ambient temperature (▲).

Figure 2 Variation of ILSS of woven glass-epoxy composites with crosshead speed at cryogenic temperature (♦), ambient temperature after cryogenic conditioning (■) and ambient temperature (▲).

Figure 3 Scanning micrograph shows no contraction of epoxy matrix of as cured specimen at ambient temperature.

Figure 4 Scanning micrograph shows contraction of epoxy matrix of cryogenically conditioned specimen.

Figure 5 Scanning micrograph shows matrix residue adhered to the fibre for cryogenically conditioned specimen.

Figure 6 Bar chart showing variation of glass transition temperature after cryogenic conditioning of the laminate.

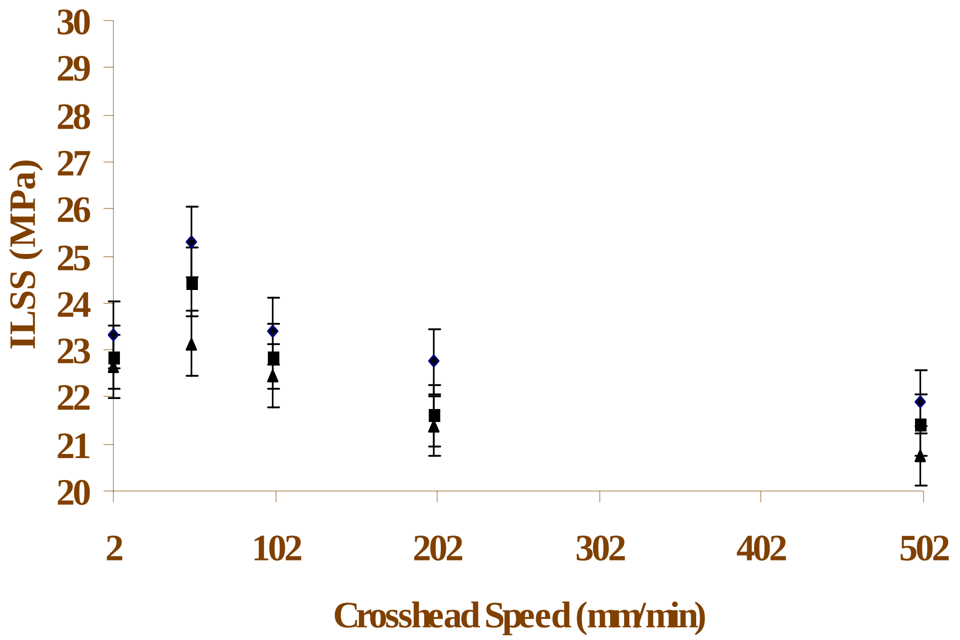
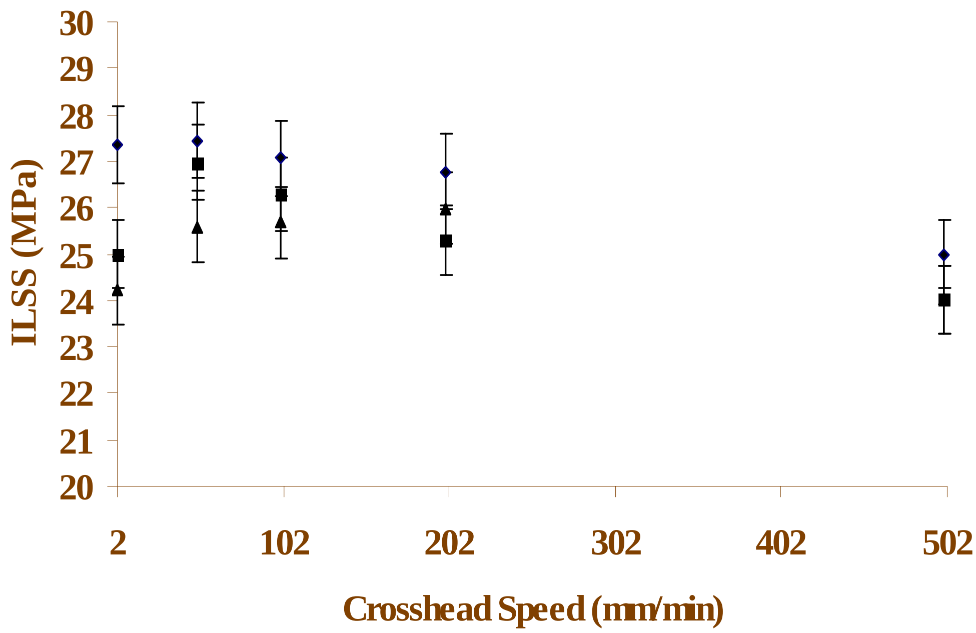

30
29
28
27
26
25
24
23
22
21
20
ILSS (MPa)
2
102
202
302
402
502
Crosshead Speed (mm/min)

Figure 1



30
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ILSS (MPa)
2
102
202
302
402
502
Crosshead Speed (mm/min)

Figure 2

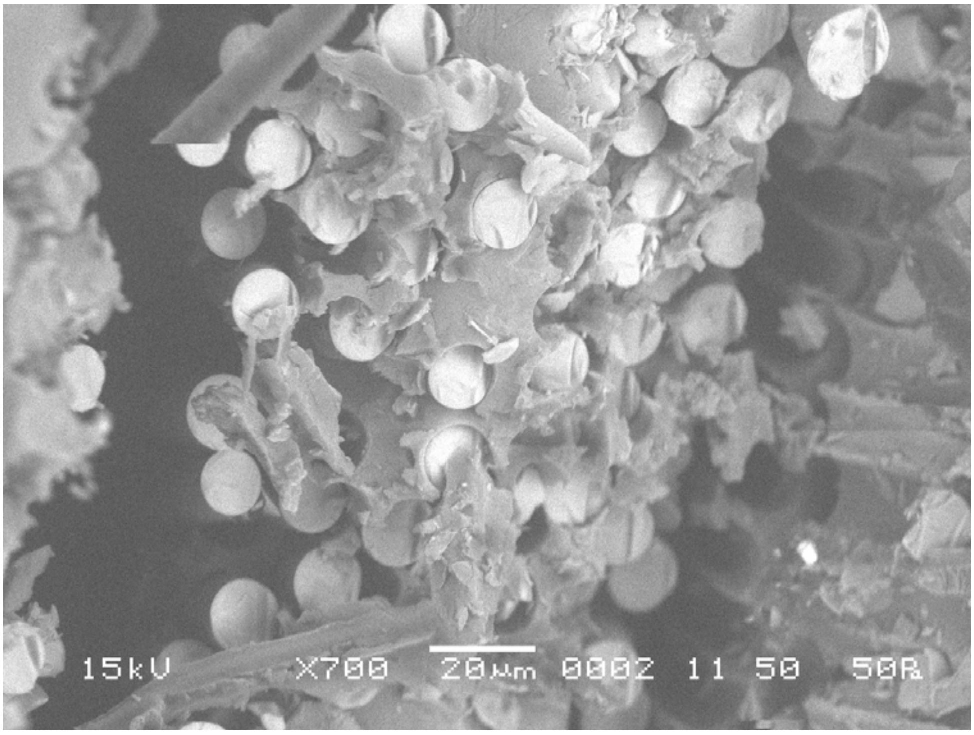


Figure 3

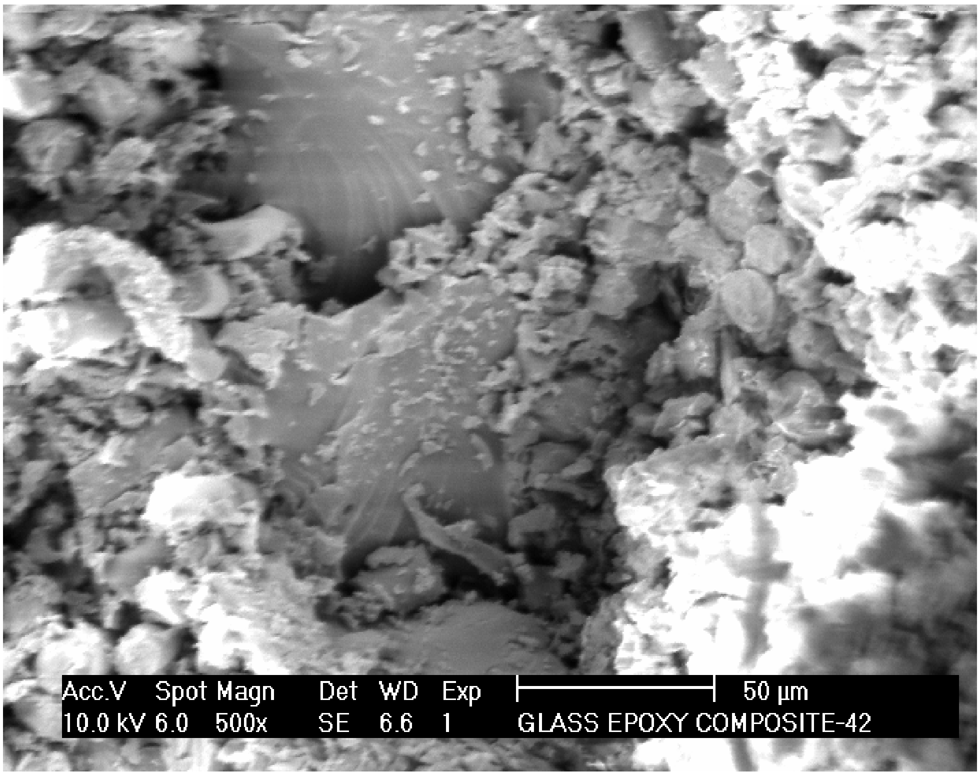

Acc.V Spot Magn Det WD Exp
50 µm
10.0 kV 6.0 500x SE 6.6 1 GLASS EPOXY COMPOSITE-42

Figure 4

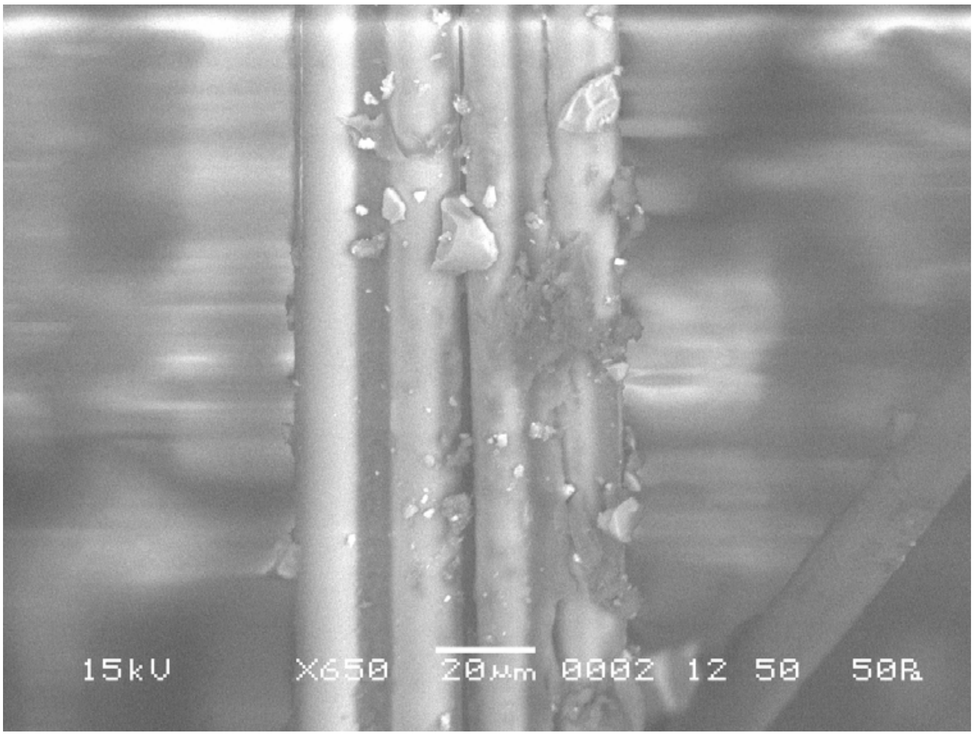
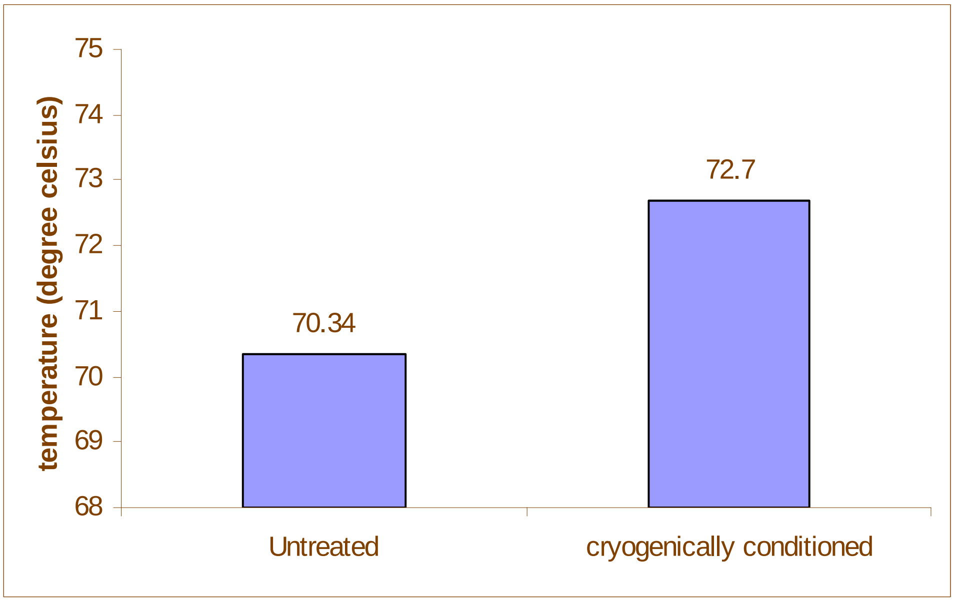


Figure 5



temperature (degree celsius)
75
74
73
72
71
70
69
68
70.34
72.7
Untreated
cryogenically conditioned

Figure 6