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Determination of glass transition temperature of ambient and cryogenically ground black pepper as influenced by moisture content and particle size

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Abstract

Glass transition temperature was determined for ambient (30°C) and cryogenically (-50°C) ground black pepper powder with reference to various moisture content (2.82-18.2%, d.b.) and particle size (85-492 μm) using state thermograms of DSC. Glass transition temperatures (T_g) were found decreased non-linearly from 139.8 to 97.1°C and 157.7°C to 91.3°C for ambient and cryogenically ground black pepper powder with respect to the increase in moisture content from and particle size at constant heating rate (10°C min^{-1}) profile. The difference of heat flow, peak point and total enthalpy of black pepper samples were also calculated.

Keywords: Ambient, Black pepper, Cryogenic, DSC, Glass transition temperature, Grinding.

Introduction

Glass transition theory has been attracting great interest in food engineering in recent years, owing to its phenomena of relating food manufacturing and preservation in a systematic way. Glass transition concept emerged in food processing in the 1980s, when Levine and Slade (1986) and Slade and Levine (1988) identified its merits in food processing and stability during storage (Rahman, 2006; Le *et al.,* 2002). Glass transition temperature is the temperature at which a substance transforms from glassy to rubbery stage takes place (Balasubramanian *et al.,* 2016). The most common plasticizer in foods i.e. water decreases the glass transition temperature (Carolina *et al.*, 2007; Carolina *et al.,* 2007 ; Enrione *et al.,* 2010). The system properties above and below the glass transition temperature differ quite dramatically and such differences have been studied exhaustively by various researchers for crystallized and viscous foods. Therefore, changes in amorphous food properties may result either from glass transition occurring because of increasing temperature (thermal plasticization) or increasing water content (water plasticization). The properties of glassy and rubbery systems may contribute to differences in physical properties (Otles and Otles, 2005), structural, mechanical and transport properties (Jaya and Das, 2009) and chemical rates (Karmas *et al.,* 1992) in each of these states. Generally, food systems are the complex mixture of carbohydrate, protein, lipids, a variety of minor components and water. Carbohydrates and protein in food system are generally miscible with water and expresses two transitions (e.g., denaturation; glass transition) and are important in understanding the relationship between food properties and it influence on food quality. Thus, the quality loss of foods is influenced by its moisture content, storage and distribution conditions too viz., microbiological growth, recovery, and death, physical changes (texture, color), chemical/biological changes (Martins *et al.* 2008). Rahman (1995) has discussed about the glass transition is a nature of second-order time–temperature-dependent transition, which is characterized by a discontinuity or change in the slope of physical, mechanical, electrical, thermal, and other properties of a material when plotted as a function of temperature. Recently, the use of differential scanning calorimeter (DSC) to observe the denaturation or gelatinization of starch has been well established (Roos, 2003). Spice

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powders during its handling, storage, processing and distribution to the final consumer, experiences a variety of temperatures and atmospheric humidity range which alters the behaviour and appearance. Black pepper is native from India and also referred as "black gold". It is a small dark brown or nearly black spherical fruits with a more or less regularly and deeply reticulate, wrinkled surface. It is mostly used for food and medicine purpose for its pungent flavour and chemical characteristics. It is used in foods as whole cracked, coarse or fine powder, and oleoresin. Furthermore, the consumer is usually very sensitive to any lumping, caking or difficulty in discharging the powder from its container, besides its flavour/aromatic and medicinal values. Hence, the knowledge of glass transition of spices as function of moisture content and particle size is essential during processing, handling, packaging and storage to prevent the caking, clumping, collapses and stickiness. The objective of this work was to determine the glass transition temperature as a function of moisture content and different particle size of ground black pepper obtained from ambient and cryogenic grinding.

Materials and methods

Materials

Black pepper seeds were procured from the local market of Ludhiana, India. The seeds were cleaned manually and broken, foreign matter, split and deformed seeds were discarded before the samples were prepared for the experiment. The initial moisture content was determined (Ranganna, 1986) and found as 8.67 %, d.b.

Sample preparation using liquid nitrogen

The matured black pepper seeds were subjected to grinding process using a pin mill (100 UPZ, Hosokava Alpine, Germany) at ambient (30°C) and cryogenic temperature (-50°C). The grinder was operated at 12000 rpm. The black pepper powder was subjected to particle size distribution studies and subjected to three grades *viz.*, 85, 284, 492 μm (ambient) and 71, 211, 322 μm (cryogenic), measured using particle size analyzer (LA 950, Horiba, Japan) (Balasubramanian *et al.,* 2013). Then, these samples were conditioned to desired five levels of moisture content (2.8-18.2 %, d.b.) for further studies.

Measurement of phase transitions

Thermal properties of black pepper powder was determined using a Digital Scanning Calorimeter (Perkin Elmer 6000, USA) operated by Pyris software. The DSC was calibrated using indium. Ground samples (5 mg ± 0.1) were placed in a hermetic sealed aluminum pans (capacity 10 μl) was heated from -150°C to 300°C with a heating rate of 10°C min^{-1}, holding at -150°C for 1 min using a empty pan as reference and nitrogen environment. All experiments were replicated thrice. The thermogram, thus obtained from DSC was analyzed further to determine the glass transition temperature. For each experimental thermogram, onset, midpoint, endpoint T_g values, ΔCp (differences in heat capacity), peak/burning point and total enthalpy were evaluated and reported.

Statistical analysis

The 3D plots and polynomial equations were performed using statistica (6.0, Stat Soft, Inc. USA) to compare the glass transition temperature with respect to moisture content and different particle size of the samples.

Results and discussion

Glass Transition

Fig. 1 represents a typical thermogram of glass transition temperature for black pepper powder, with a T_g value at 97.7ºC (midpoint value) for the cryogenic sample of 492 μm particle size. The onset, midpoint and endpoints of glass transition were also determined from DSC thermogram. It is noted that the peak points or burning point of the samples were obtained in the range of 150 to 160°C.

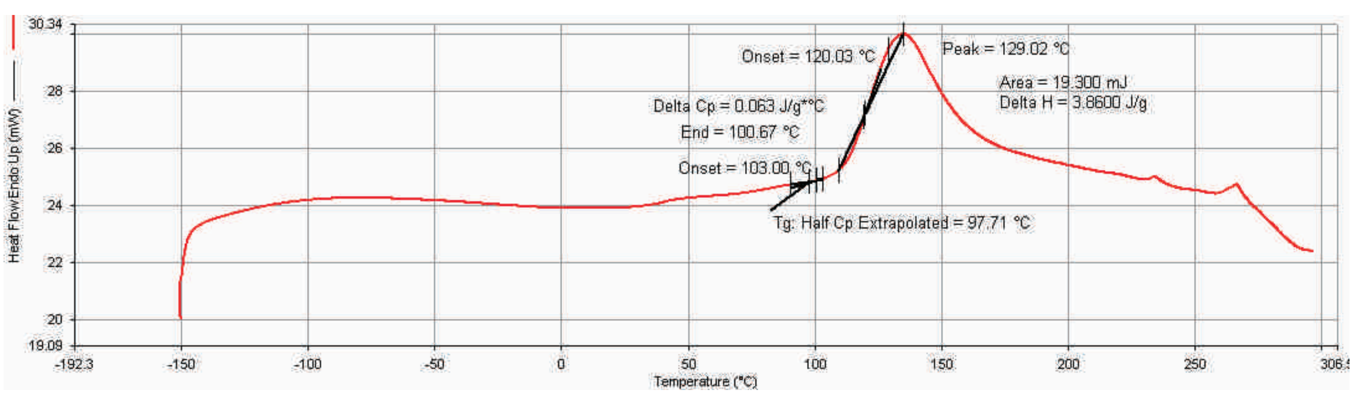


Fig. 1 A typical thermogram of black pepper powder (492μm) using differential scanning calorimeter (DSC)

Effect of moisture and particle size on T_g

Figs. 2-4 also shows the three dimensional quadratic views of T_g values with respect to moisture content and different grade size of ambient (85, 284 & 492 μm) and cryogenically (71, 211 & 322 μm) ground black pepper, respectively. It shows a significant decrease in T_g both conditions from 157 to 91°C over when moisture content increased from 2.8 to 18.2 % (d.b.) as well as increasing of their grades. The relationship between glass transitions temperature and other thermal properties of both conditions (onset, midpoint and endpoint) with moisture content and grades can be expressed as non-linear models (Table 1). Since the water molecules acts as plasticizers, it could be attributed that the higher moisture content showed a decreased value of $T_{g.}$ Enrione et al., 2010 also observed a decreasing trend in Tg from ~170°C to ~25°C in starch samples for the moisture content increase (5-25% w.b.) Similarly, Kalichevsky *et al.* (1993) measured a decrease of T_g (110°C) for the 10-20% (db) increase in moisture content in waxy maize starch. Similar behaviours were reported by Zeleznak and Hoseney (1987) for wheat starch up to 25% moisture content. However, it was also reported that there is no substantial decrease in T_g for samples greater than 25 % w.b. moisture content suggesting the formation of separated water rich fraction which does not contribute to a further decrease in the polymer T_g. This behaviour corroborates with the dependency of T_g on the molecular weight and decrease of average molecular weight of the mixture. Also the notion that the free volume is increased by the addition of water can also contribute to the decrease of transition temperature (Slade and Levine 1993).

Table 1. Models expressing the differential thermal properties with respect to grade and moisture of ground black pepper

Properties	Model	(R^2)
Ambient grinding		
T_g (onset)	$4.25\times10^4+107.56M+823.22G0.38M^2-0.98MG-3.98G^2$	0.90
T_g (midpoint)	$-3.18\times10^4+51.94M+623.04G-0.27M^2-0.46MG-3.04G^2$	0.91
T_g (endpoint)	$-4.56\times10^4+88.65M+890.94G-0.33M^2-0.81MG-4.34G^2$	0.94
Δ Cp	$-2.42\times10^3+6.09M+47.09G-0.004M^2-0.059MG-0.229G^2$	0.92
Peak	$-3.44\times10^3+76.74M+62.58G-0.215M^2-0.709MG-0.269G^2$	0.95
Δ H	$-5.71\times10^4+9.67M+1.12\times10^3G+0.047M^2-0.101MG-5.49G^2$	0.90
Cryogenic grinding		
T_g (onset)	$-1.86\times10^5+128.07M+3655.33G-0.19M^2-1.24MG-17.91G^2$	0.92
T_g (midpoint)	$-1.26\times10^5+126.09M+2475.26G-0.10M^2-1.24MG-12.12G^2$	0.95
T_g (endpoint)	$-1.41\times10^5+190.59M+2767.95G-0.13M^2-1.87MG-13.52G^2$	0.93
Δ Cp	$-1.27\times10^3+7.71M+23.91G+0.0049M^2-0.077MG-0.112G^2$	0.96
Peak	$-1.36\times10^5+101.28M+2669.99G-0.109M^2-0.988MG-13.08G^2$	0.93
Δ H	$-1.02\times10^5+96.12M+1993.11G+0.0019M^2-0.937MG-9.74G^2$	0.92

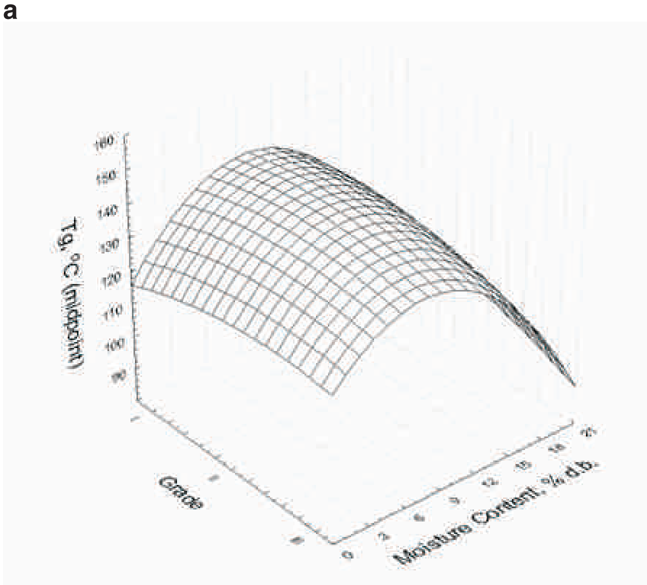
where, Tg = glass transition temperature, °C; M = moisture content, %, d.b.; G = particle size grade, μm; ΔCp = change in heat capacity, J/g°C; ΔH = total enthalpy, J/g.

Comparison of T_g with other thermal properties

Figs. 5-7 shows the trends of change in heat capacity, peak/burning point of samples and total enthalpy of black pepper powders were obtained from DSC thermogram results. The thermograms of DSC for all the samples showed a decrease in T_g above 6 % moisture content. The average value of Δ Cp, peak point and ΔH values decreased with the increase in moisture content and their different grades and varied from 2.03-0.023 J/g°C, 176.14-135.12 °C and 33.53 -5.43 J/g for ambient and 2.34-0.014 J/g°C, 183.16-115.92 °C and 33.21-3.93 J/g for cryogenic conditions, respectively. Figs. 2-4 shows the effect of water plasticization causes a significant decreases inT_g and other properties with increase in moisture content. Similar results were reported for glass transition temperature by Enrione *et al.,* 2010. Kalichevsky *et al.* (1993) measured a decrease of 110 °C when the moisture content was increased from 10 to 20 % (db) in waxy maize starch. When m.c was increased from 9 to 15% T_g was decreased 155 to 97 ºC, and 145 to 91 ºC for both ambient, cryogenic respectively. From the results, it could be understood that for very low moisture content at 3 %, d.b. (i.e., high solids) there exist a decrease of T_g with the increase of solids. Thus, moisture content decrease from 6 to 3%, d.b., decreased the T_g from 139 to 138 ºC and from 158 to 145 ºC for ambient and cryogenic samples, respectively. Similar results were obtained by Rahman *et al.* (2010) with spaghetti samples for moisture content. Figs. ii-iv also showed the dependency of T_g upon the particle size. It is showed that for a lower particle size (85 µm) there exists a sudden decrease after the 10 % for both ambient and cryogenic samples.

It is found that the T_g is comparatively higher for the cryogenic samples and the glass transition temperature along with other thermal properties also decreased with the increase in moisture content and size grades as a key observation. Wang *et al.,* 2009 reported the other possibilities which affect the quality and the stability of the food products. Bindzus *et al.,* 2002 detected a similar T_g vs moisture content profile for extruded corn, wheat, and rice starches. Also, evidence has shown that the cryogenic grinding retains the nutrition qualities of the materials. Molecular mobility increases 100-fold most stable below its glassy state (Rahman *et al.*, 2010). Lourdin *et al.* (1997a, b) also studied the influence of glycerol and water on the structure and mechanical properties of potato starch extrudates, discussed the hypothesis of the presence of polymer and plasticizer-rich phases in terms of a relation between the T_g of each phase, their ΔCp, and the fractions of each component present. The same authors propose a molecular state where the plasticizer concentration reaches a limit (sorption sited of the polymer occupied by water and plasticizer molecules), above which plasticizer–plasticizer interactions can occur leading to the formation of polyol rich fractions in the matrix. For this particular case, a glycerol-rich fraction would have the potential to attract water from the matrix affecting the overall T_g of the mixture even further. Thus, corroborating the above findings, it may be concluded that the low value of carbohydrate in samples reduced the T_g values. Results can be made that the cryogenic grinding is best suited for the retention of nutritional quality and also this effect is related with the stability of the product.

a



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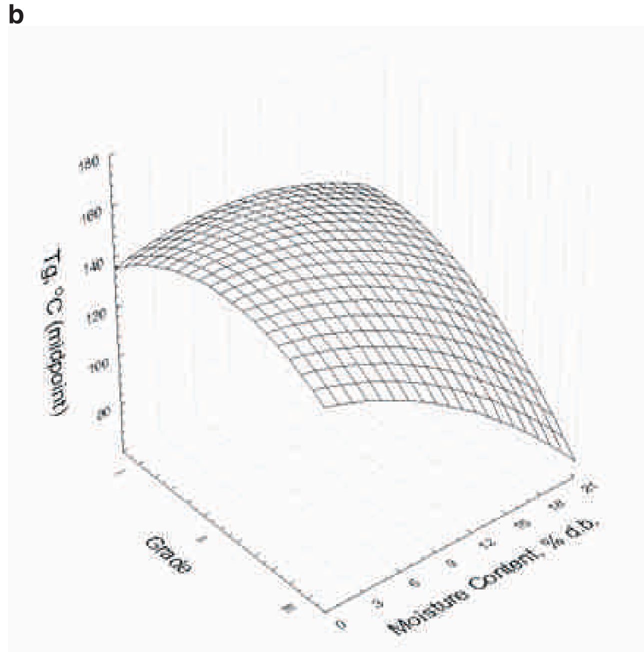

Fig. 2 Variation of glass transition temperature (midpoint) with moisture content and different grades (a) Ambient (b) Cryogenic grinding conditions

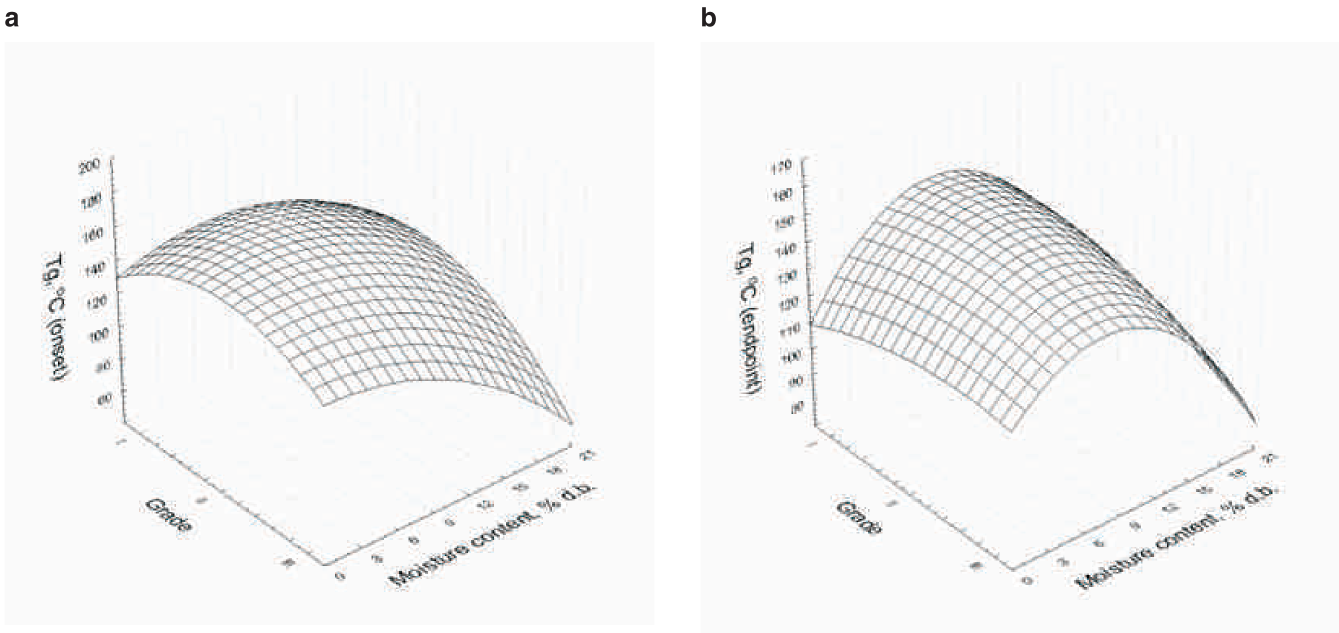

Fig. 3 Variation of glass transition temperature (onset) with moisture content and different grades (a) Ambient (b) Cryogenic grinding conditions

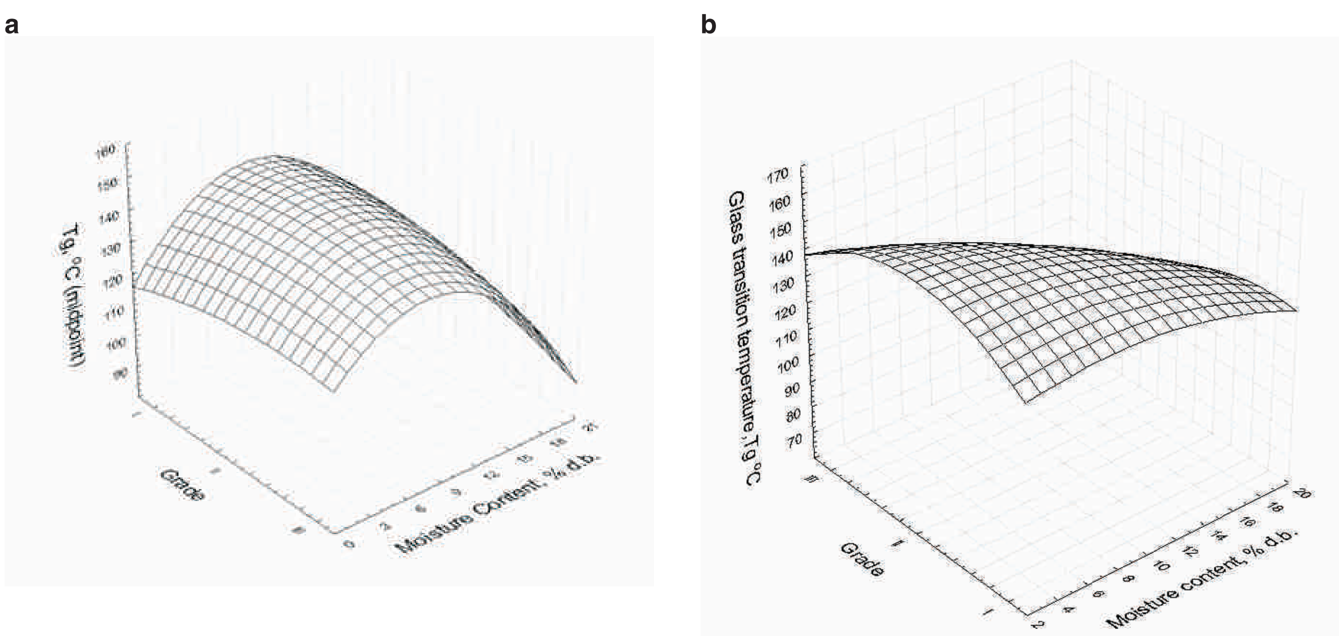

Fig. 4 Variation of glass transition temperature (endpoint) with moisture content and different grades (a) Ambient (b) Cryogenic grinding conditions

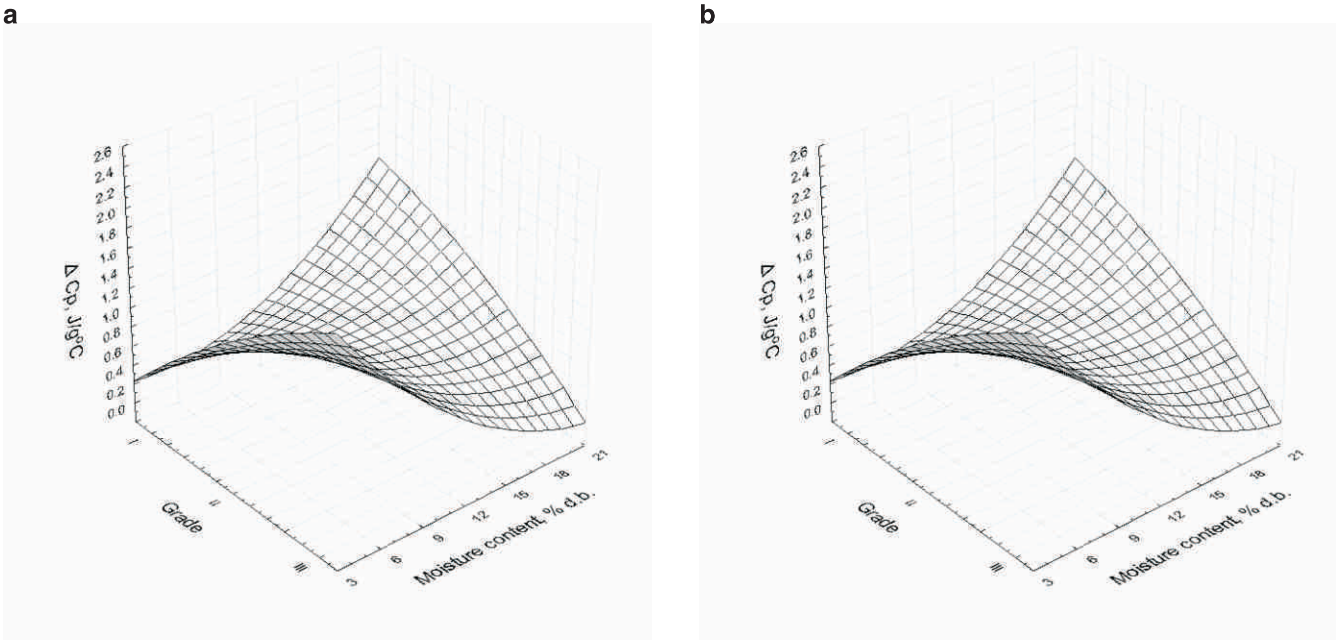

Fig. 5 Variation of ΔCp (change in heat capacity) with moisture content and different grades (a) Ambient (b) Cryogenic grinding conditions

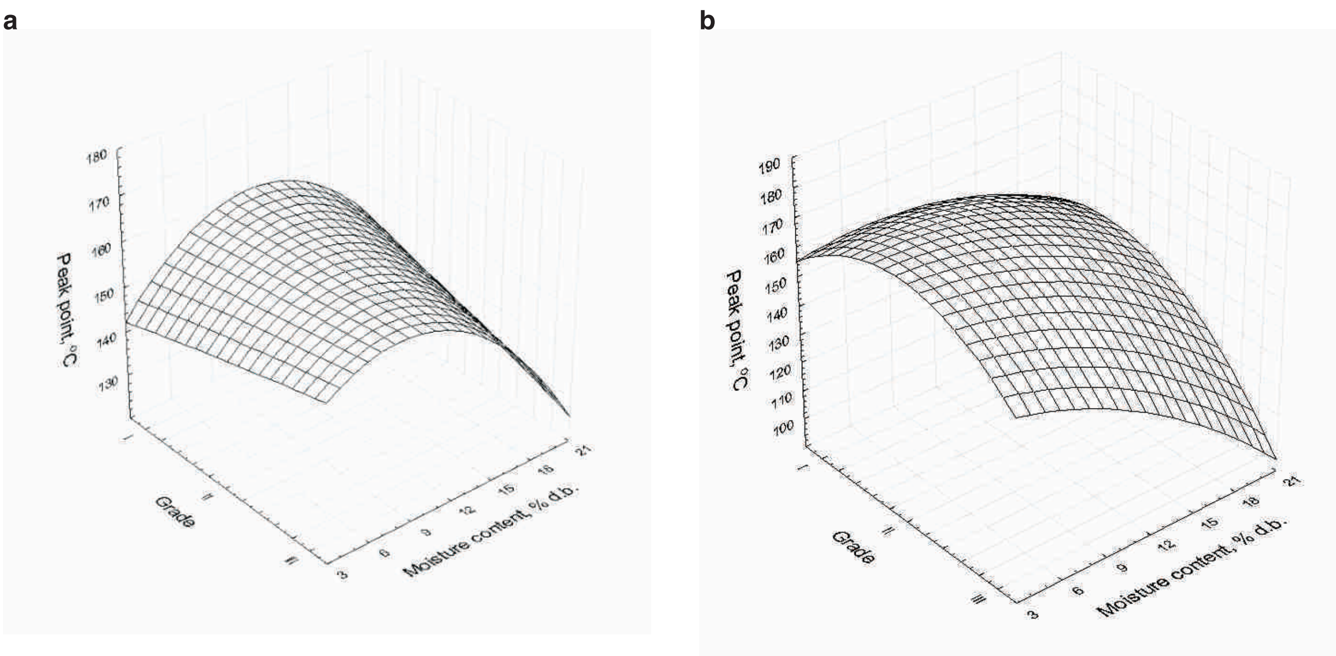

Fig. 6 Variation of peak point/burning point of samples with moisture content and different grades (a) Ambient (b) Cryogenic grinding conditions

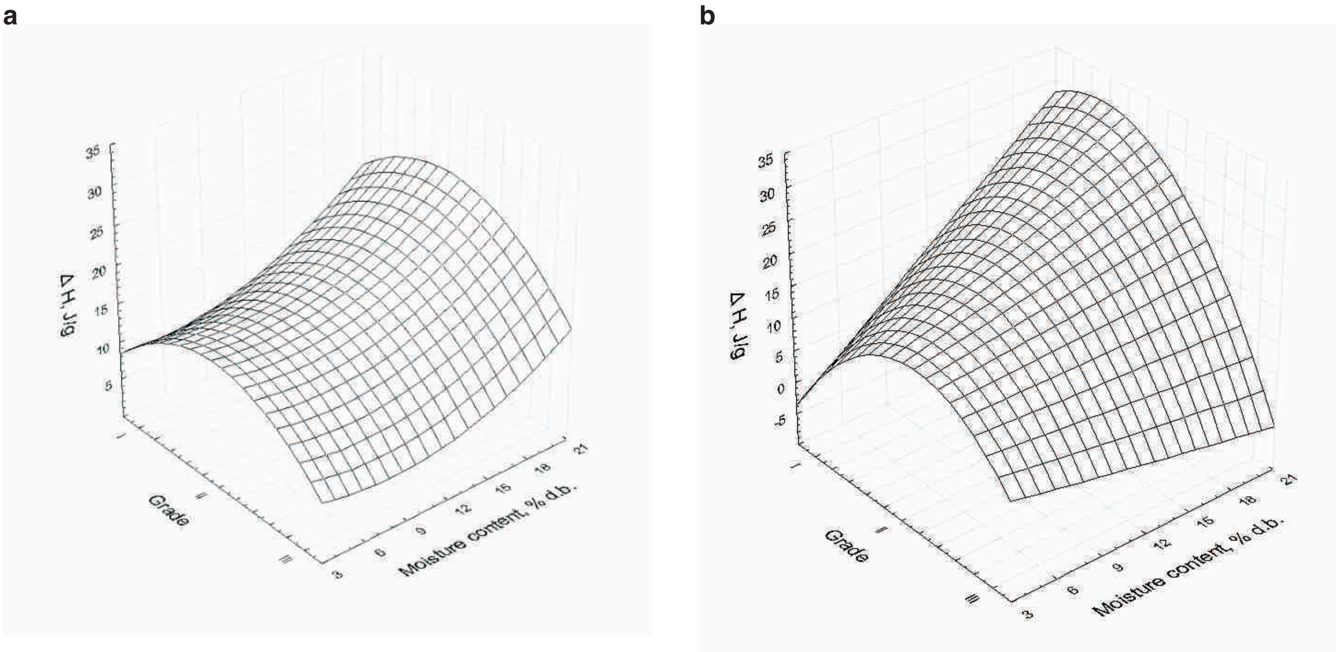

Fig. 7 Variation of ΔH (total enthalpy) with moisture content and different grades(a) Ambient (b) Cryogenic grinding conditions

Conclusions

In this work, T_g of ambient and cryogenically ground black pepper samples were showed a reducing trend with moisture content. The glass transition temperature was found higher for cryogenically ground samples as compared to the ambient grinding of black pepper. There were significant decrease in the glass transition temperature with the increase in moisture content and particle grades between ambient and cryogenically ground samples. Other thermal properties (ΔCp, Peak point and total enthalpy) also followed a same trend with the increase in moisture content and size grades of black pepper ground at ambient and cryogenic conditions.

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