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Thermal and Microstructural Property of Extruded Snack: An Overview

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Abstract
Rice and Chapra ***(Fenneropenaeus indicus)*** mixture were extruded using a co rotating fully intermeshing twin-screw extruder to prepare carbohydrate protein based snack. The aim of the present work is to study the glass transition temperature and microstructural behaviour of carbohydrate-protein extrudate snack. Parkin Elmer Differential Scanning Calorimeter method was used for studying phase transition behaviour of complex carbohydrate-protein extrudate at a heating rate of 5ºC/min and in the temperature range - 80ºC to 180ºC. On the other hand, Scanning Electron Microscope (SEM) was used to study the microstructural behavior of multicomponent extrudate at an accelerating voltage of 20 kV and at 1000 X magnification. State diagram indicated phase separation of carbohydrate-protein complex food system at macromolecular level. The glass transition temperature of protein dictated the texture of the mixed system. At room temperature, extrudate with 15% moisture is glassy while extrudates obtained <15% moisture shows rubbery texture and higher moisture profile shows burnt texture. Microstructural analysis performed by SEM shows typical network like structure at 150°C and 15% moisture.
Keyword: Shrimp, fish protein, extrusion, Differential Scanning Calorimeter

I. Introduction

The challenge in the field of food research is to produce unique, innovative products based on current market demands. Extrusion cooking is such a common processing effort for converting starchy and proteineous material into fabricated products at high temperature short time duration to produce expanded snacks. Starchy materials are generally used for production of snacks. However, carbohydrate-fish protein mixtures are rarely explored for production of snack food by extrusion. Chapra ***(Fenneropenaeus indicus)***, a local variety of shrimp has been used as food items in the coastal areas of West Bengal, India. Chapra contains approximately 20% protein, 1% fat, 76% moisture, 1.5 % ash and a good amount of minerals. (USDA National Nutrient Database for Standard Reference, Release 15, 2002).A large amount of Chapra is wasted every year due to lack of proper preservation measures. Considering advantages of twin screw extrusion process, coastal Chapra and rice flour mixture were extruded to improve the nutritional quality of extruded product and to study the related functionality of complex carbohydrate and shrimp-protein mixture.

Glass transition temperature is critical parameter, which control the extrudate processability, properties, stability and safety for the amorphous food matrices (Slade and Levine, 1993; Roos et al, 1995, D'Cruz and Bell, 2005). One of the major factors that control the glass transition of food system is the water content. (Roos and Karel 1991; Lillie and Gosline,1993; Brent et al 1997). The phase behaviour of simple food systems, particularly starchy food has been extensively studied in the literature. However, the majority of foods have a much more complex composition, with a protein carbohydrate polymeric matrix that entraps low mass molecular weight components like fats, sugars and others. The properties and storage stability of carbohydrate-protein mixtures can be controlled if the phase behavior and the influence of intrinsic and external factor on this behaviour are well understood. (Matveev et al.2000). Microstructural analysis is another important phenomena to identify the change in molecular structural arrangement after high temperature short time extrusion processing.

The objective of the present study is a) to analyse the glass transition behavior of carbohydrate protein comlex system to find out the system behavior for food process design b) to examine the surface morphology of the extrudates through Scanning Electron microscopy.

II. Materials and Method

Materials: Rice (*Oryza sativa L)* procured from local market and Chapra (*Metapenaeopsis stridulans*) collected from coastal areas of West Bengal and Table salt (2%) (Tata) procured from local market was used for control formulation.

Preparation of Feed for extrusion: Chapra collected from coastal area was washed thoroughly with fresh water and the water was drained and then it was dried in an oven (800 W grill oven Sanyo, JP) at 60°C for 2 hours. Rice collected from local market was also washed and dried at the same condition. After the water was completely removed, dried shrimp and rice were finely ground into powder form with a blender (Mixer Grinder, Bajaj,GM-550) separately. Rice and Chapra powder thus prepared was mixed (5:1) mixture. The flour was sealed in polyethylene bags & stored at 4°C in refrigerator for 48 hours prior to extrusion. The moisture was adjusted to 11%, 13%, 15% and 17% adding the required amount of water to the flour mixture and conditioned

III. Extruder & Extrusion cooking

A co-rotating fully intermeshing twin screw extruder was used (screw profile 12:1 barrel length 350 mm; barrel bore diameter 38 mm; screw diameter 37.8 mm; conveying angle 30°; intermeshing screws 24 mm apart) for extrusion of the feed mixture using a 3 mm diameter die. The screw speed of the extruder was set at 475 rpm, while the feed rate was maintained constant at 28g/min. The extruder started functioning properly with said feed mixture at 110°C and at 11% feed moisture condition and totally stopped after 170°C and at 19% feed moisture condition. The temperature of the extrudate at the time of product discharge was at 110°C, 130ºC, 150°C &165°C respectively and the feeding material moisture content were 11%,13%15% and 17%. Phase behaviour of the extrudate was studied.

Moisture content: Moisture content of control and extruded products were measured using standard hot air oven (Model No-06104, SC Dutta & Co, Kolkata) according to AOAC, 2002.

Shear strength: A universal Texture Analyzer was used in compression mode to record the required force to break extruded products. The extruded samples (5cm long) was placed on the platform transversally over a metal sheet support (1cm. thick) and operated in a compression mode with a sharp testing blade (3mm. Thick, 6.93 mm wide). The texturometer head moved the probe down at a rate of 15 mm/min until it broke the extrudates. Values reported were averages of 30 measurements using load of 50N.

IV. Microstructure Analysis

Scanning Electron Microscope (SEM):

Scanning electron microscope (Jeol, JSM 5200, Tokyo, Japan) was used at an accelerating voltage of 15 kV to view extrudate in three dimension and to determine the shape and surface feature of extrudate. Extrudates from all the treatments and the control sample were mounted stubs with adhesive tape and sputters coated gold approx 190 Aº thick for 2.5 min at 10 mA before observation with SEM. One micrograph was taken for at 1000 X magnification for the sample. All the images for each sample showed representative result.

V. Differential Scanning Calorimeter:

A Perkin Elmer Instron Pyris Diamond Differential Scanning Calorimeter (DSC) was used to make T_g measurement. The calorimeter was calibrated at a heating rate of 5ºC/min. Small discs of 15-20 mg of samples were inserted in medium pressure, stainless steel crucible (which did not allow any moisture loss during the measurement). The samples were scanned at a heating rate of 10ºC/min in the temperature range - 80ºC to 180ºC. The data was processed with Pyris software in Microsoft Windows 98 system.

Statistical Analysis

Experimental data were analyzed using STATISTICA for Windows Release 9, Stat Soft Inc. 2009 and Microsoft Excel 2003 version.

VI. Result & Discussion

Microstructure analysis

Microstructure analysis performed by SEM indicated heterogeneous, network like matrix with voids at different temperature and moisture condition (Figure 1A to Figure 1E). Figure 1A distinctly shows two different size granules indicating two different types granule of shrimp and carbohydrate. Some disrupted nonsymmetrical structure and shear in the granule was found in the extruded feed at 120 °C in Figure 1B. SEM picture at 135°C shows better symmetrical arrangement of carbohydrate and protein network than 120°C (Figure 1C). SEM picture at 150ºC shows continuous network like structure in a symmetrical fashion in (Figure 1D). SEM picture of the extrudate at 165°C (Figure 1E) temperature indicated maximum shear in the granules i.e damage and breaking in continuous symmetrical structure was observed. SEM picture at 120°C shows unsymmetrical pattern and holes.SEM result shows more symmetrical fashioned network like structure extrudate produced at 150° C and 15% moisture condition and after the limiting temperature crosses the structure break down. Thus most expanded product was observed at 150°C. Absence of starch granule in all SEM pictures of the extrudate indicated gelatinization.

Phase transitions in the rice - shrimp (carbohydrate - protein) extrudate:

Glass transition temperature shows low even nil effect with the change of extrudate process temperature, whereas significant change of glass transition temperature with the change of process moisture was studied. Thus in the present study, the phase behaviour at optimum temperature (150°C) and four different process moisture condition (i.e 11, 13,15,17%) for the extruded system is discussed. T_g value of protein plays an important role in controlling extrudate shrinkage and cellular damage (Alavi et al, 1999).

The glass transition behaviour of rice flour extrudate at 11% process moisture condition is represented in fig. 2. Fig.2 indicates inflection point at 56°C (55.649°C); onset temperature (i.e. the temperature at which inflection started) was noted at 54°C (53.994ºC) and C_P value at 0.218 J/g/ºC. Thus glass transition temperature of rice flour was 56ºC.

Baseline of DSC thermogram of rice and Chapra extrudate at 11% moisture is represented in (Fig. 3). Baseline in Fig. 3 indicates two-inflexion point (T_g value), which in turn reveals two glass transition temperatures in carbohydrate-protein complex food system.

Here, T_g value of extrudate at 11% moisture condition, (noted from Fig.3) was 54.2ºC, C_P value at 0.177j/kg, and onset value at 53.3°C. Fig. 4 shows inflexion point at –11.147ºC and C_P value was 0.189J/g and Onset value i.e inflexion starting temperature was at –2.874°C. Fig. 4 & Fig.5 corresponds the two T_g value at 11% moisture content and resembles the T_g values of rice sample in Fig.2 which in turn indicates that glass transition temperature of the rice sample in rice shrimp extrudate, and marked as $T_{g1.}$ Thus, T_g value of extrudate at 11% moisture content in Fig.5 indicates glass transition temperature of protein sample in rice-shrimp extrudate and marked as T_{g2}. Thus, T_g analysis of carbohydrate and shrimp extrudate shows two separate T_g and phase behaviour of extrusion process of carbohydrate and protein mixture distinctly explains phase separation of two biopolymer at macromolecular level.

The protein glass transition temperature for the extrudate processed at 13%, 15% & 17% process moisture condition represented in Fig.6-Fig.8. T_{g2} value at 13% process moisture condition in (Fig. 6) shows inflection point at –21ºC (21.150°C), C_P value at 3.531e $^{-0.002}$ J/g/°C onset was noted at –19.269ºC . T_{g2} value at 15% moisture condition in Fig 9 shows inflexion point at –36°C (-36.105°C) where inflexion started at 19°C(-19.262°C) and C_P value was 0.204 J/g/°C. T_{g2} value at 17% moisture condition in Fig 10 shows inflexion point at –27°C (-26.700°C) where inflexion started at 28°C(-27.743°C) and C_P value was 0.175 J/g/°C.

Very few T_g values have been reported in the literature specially on protein system. T_g values reported in the literature for beef are also very contradictory ranging from (-60) to (-5)º C (Brake and Fennema 1999) and for meat -23ºC. In the present study, glass transition temperature varies from (-11ºC) to(-36°C) as evident from above results. Location of protein glass transition controls the physical state of product. (Morarue et al, 2002). Thus, T_{g2} values shows decreasing trend with increase in moisture content from 11%-15% whereas at 17% slight increase in glass transition temperature was noted.

When the product temperature (T_p) is above T_g+ bubble temperature (here, -36ºC) (i.e highest glass transition temperature (T_g) where most expanded product obtained), the cell wall viscosity is low enough for bubble growth or shrinkage. (Della Valle et al, 1996; Fan et al, 1994) Differential Scanning calorimetry (DSC) experiments indicated that T_g of Chapra (shrimp) protein at control formulation (with 15% moisture after which bubble starts to collapses), as it exited the die, was about (-36°C) while the temperature at the product discharge zone was 150°C and product temperature (T_p) was maintained at 50°C. This caused the extrudates to shrink as the air inside the cells cooled down and contracted. The cells increased in size as long as T_p remained greater than T_g+36°C, but at a certain critical cell size, the cell walls reached their maximum extensibility (specially when barrel temperature was 170°C), beyond which they ruptured and the extrudate structure damaged and increase in protein T_g value was also observed. When the oven exit temperature was 135°C or 170°C, the structure was set before this critical cell size could be attained, thus no rupture of cells was observed. Here in the present study also, all the process temperature was so chosen that product temperature always shows higher value than that of protein glass transition temperature (Tg_2) to obtain product with less structural damage. Thus, T_g value shows significant impact in food product design. The extrudates obtained at 11%, 13% & 17% moisture condition shows rubbery texture and lower expansion volume at room temperature compare to that of the product obtained at 15% moisture. This behaviour is clearly explained from Tg_2 value at different process moisture condition. T_{g2} value at 11%, 13% and 17% process moisture condition is higher than that of the Tg_2 value at 15% process moisture condition and thus the difference with product temperature (50°C) is higher at 11%, 13%and 17% than that of at 15% process moisture condition and as a result, product shows different characteristic than that of obtained at 15% moisture

(i.e optimum process moisture condition). This is clearly explained in the present study, where it was estimated that T_g+36ºC values at 11%, 13% and 17% moisture conditions are 25°C, 15°C & 9°C (as T_g value correspond to -11°C, -21°C & -27°C respectively at 11%, 13% and 17% moisture condition) which is lower than product temperature (50°C) and higher than the T_g+36ºC value obtained at 15% process moisture condition (0°C) (as T_g value at 15% moisture condition was at -36°C). Thus, at 15% moisture condition, the difference of product temperature (T_p-50°C) with T_g+36ºC value (i.e 0°C) is highest and highest increase in cell size was observed which in turn predict highest expansion volume at that process moisture condition. Thus, extrudates obtained at 15% moisture condition are typical glassy polymers, while the extrudates obtained at lower and higher moisture condition become rubbery. Thus, the location of the protein glass transition temperature (T_{g2}) controls the physical state of the product. (Alavi et al, 1999).
Upon direct examination by texture analyzer, the product obtained at optimum temperature condition (at 150° C) and 15% moisture condition were found brittle and glassy as also evident from lowest shear force value (14.12 N) (Table 1), while the extrudate obtained at 11, 13 & 17% moisture (Shear force value of 19.12, 15.76, 14.52 N respectively as recorded from Table1) was rubbery. In the present study, the most expanded, greatest volume and lowest stress were obtained at 150ºC barrel temperature and 15% moisture. The determined shear force value of the extrudate varies between 14.12-28.82 N.

Thus T_{g2} value of protein dictated the physical state of the product. The same also validated with the shear force value obtained by texture analyser. Protein glass transition temperature has significant impact on food product design and process control.

VII. Conclusion

In the carbohydrate –protein complex extruded system, starch and proteins were immiscible and retained their own glass transition. The immiscibility of the system was clearly illustrated on thermogram with two different glass transition temperatures. Texture of matrix was dictated by the location of the protein phase glass transition. Thus the state diagram provides valuable information, which can be used as predictive tools for food product design. Microstructural analysis performed by Scanning Electron microscopy revealed symmetrical fashioned network like structure at 150°C and 15% moisture.

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References

[1] Alavi, S.H., B.K. Gogoi, M. Khan, B.J. Bowman and S.S.H. Rizvi, 1999. Structural properties of protein-stabilized starch-based supercritical fluid extrudates. Food Res. Int., 32: 107-118. http://www.ingentaconnect.com/content/els/09639969/1999/00000032/00000002/art00063

[2] Brake NC. Fennema 1999. Glass transition values of muscle tissue .J Food Sci 64 (1):10-15

[3] Brent, J.L., S.J. Mulvaney, C. Cohen and J.A. Bartsch, 1997. Thermomechanical glass transition of extruded cereal melts. J. Cereal Sci., 26: 301-312. http://www.sciencedirect.com/science/article/pii/S0733521097901405

[4] D'Cruz, N.M. and L.N. Bell, 2005. Thermal unfolding of gelatin in solids as affected by the glass transition. J. Food Sci., 70: E64-E68.

[5] Della Valle, G., P. Colonna, A. Patria and B. Vergnes, 1996. Influence of amylose content on the viscous behavior of low hydrated molten starches. J. Rheol., 40: 347-362.

[6] Fan, J., J.R. Mitchell and J.M.V. Blanshard, 1994. A computer simulation of the dynamics of bubble growth and shrinkage during extrudate expansion. J. Food Eng., 23: 337-356.

[7] Lillie, M.A. and J.M. Gosline, 1993. The Effects of Swelling Solvents on the Glass Transition in Elastin and other Proteins. In: The Glassy State in Foods, Blanshard, J.M.V. and P.J. Lillford (Eds.). Nottingham University Press, Loughborrough, Leicestershire, pp: 281-302.

[8] Matveev, Y.I., V.Y. Grinberg and V.B. Tolstoguzov, 2000. The plasticizing effect of water on proteins, polysaccharides and their mixtures. Glassy state of biopolymers food and seeds. Food Hydrocolloids, 14: 425-437.

[9] Moraru C.I., Kokini J.LNucleation and Expansion During Extrusion and Microwave

Heating of Cereal Foods, Comprehensive Reviews In Food Science And Food Safety 2003—Vol. 2, 120-138

[10] Roos, Y. and M. Karel, 1991. Water and molecular weight effects on glass transitions in amorphous carbohydrates and carbohydrate solutions. J. Food Sci., 56: 1676-1681.

[11] Slade, L. and H. Levine, 1993. Water relationships in starch transitions. Carbohydr. Polym., 21: 105-131.http://www.sciencedirect.com/science/article/pii/014486179390006P

[12] USDA National Nutrient Database for Standard Reference, Release 15 (August 2002)

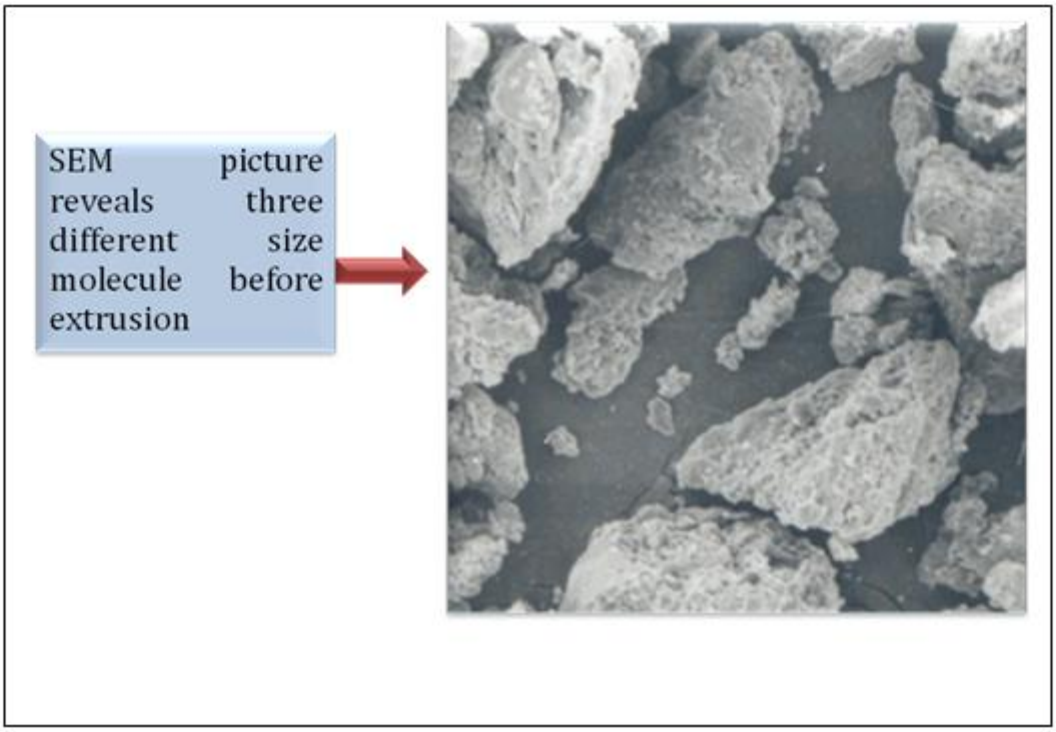

Fig 1A: SEM picture of Rice & Shrimp Protein unextruded

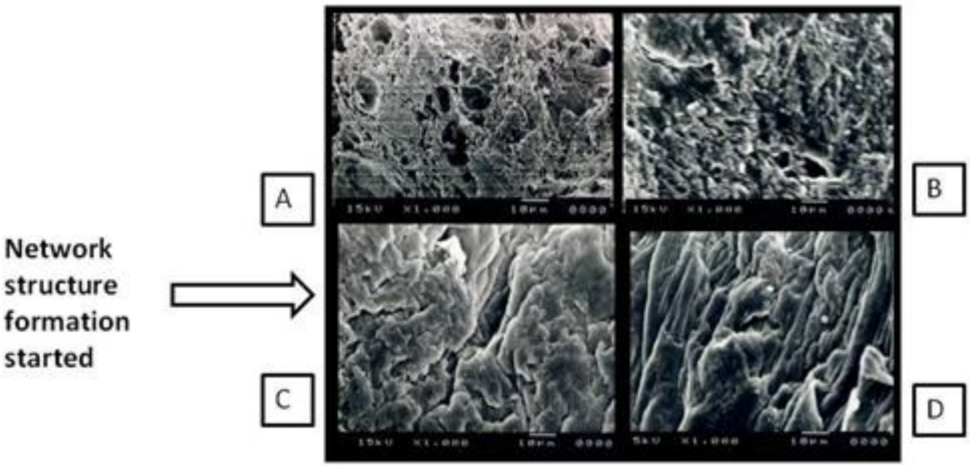

Figure 1B: SEM picture of Rice & Shrimp protein Extrusion at 120 °C B) 11% C) 13% D) 15% E) 17% moisture

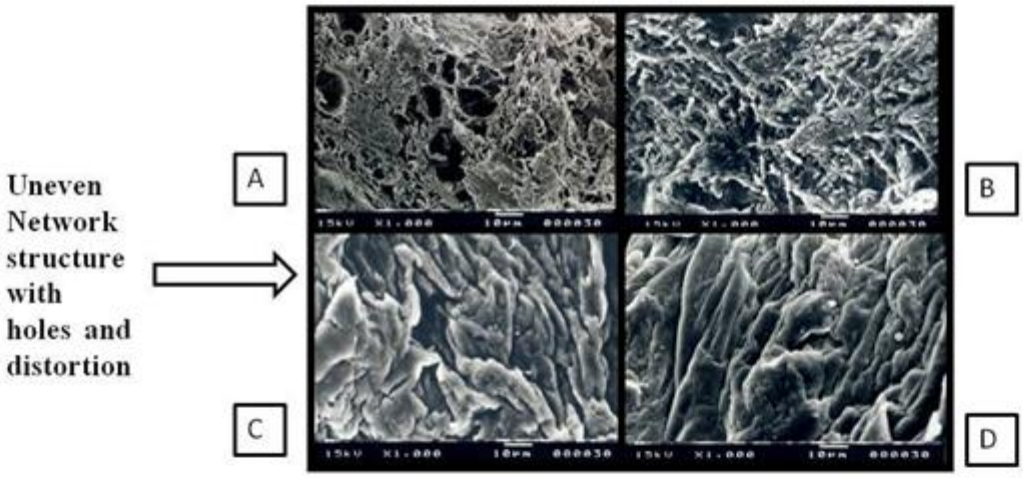

Fig. 1C : SEM picture of rice & shrimp protein extrusion at 135°C a) 11%, B) 13% C) 15% D) 17% moisture

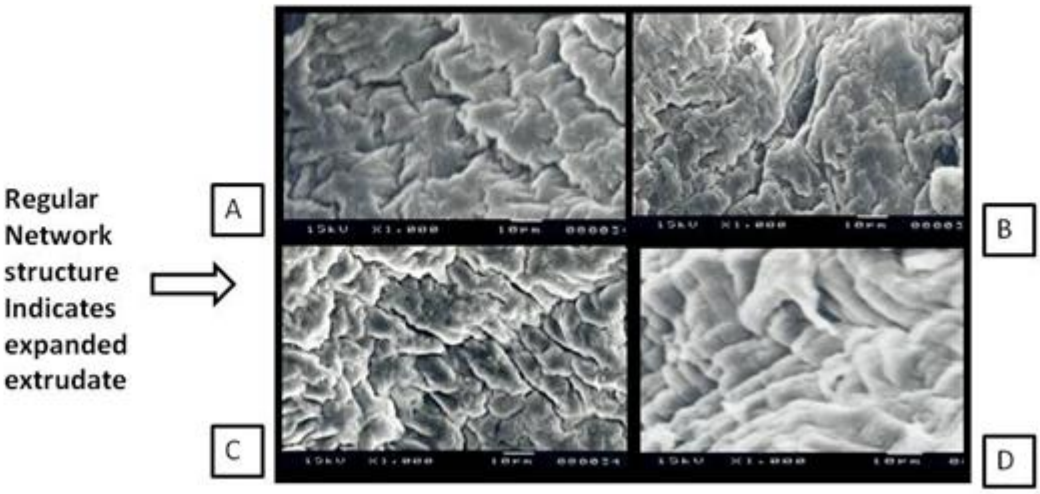

Fig.1D: SEM picture of rice & shrimp protein extrusion at 150°C a) 11%, B) 13% C) 15% D) 17% moisture

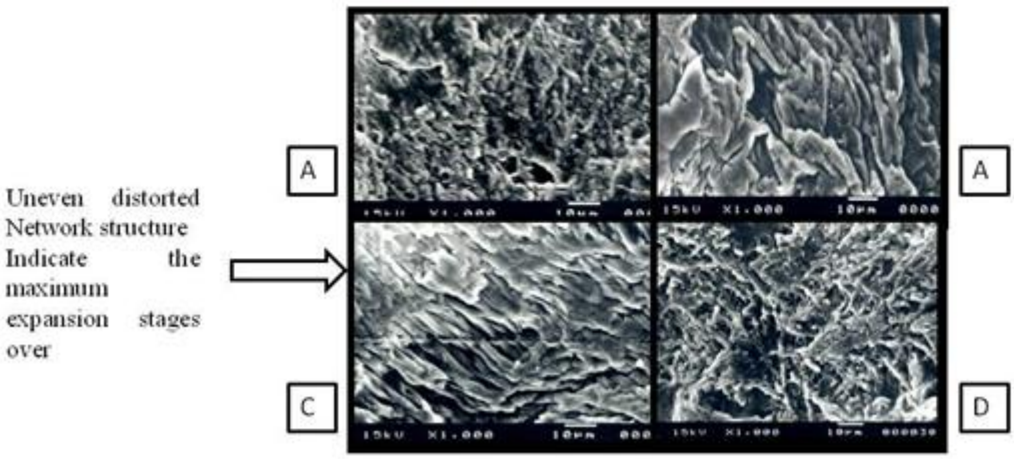

Fig. 1E: SEM picture of rice & shrimp protein extrusion at 165°C a) 11%, B) 13% C) 15% D) 17% moisture

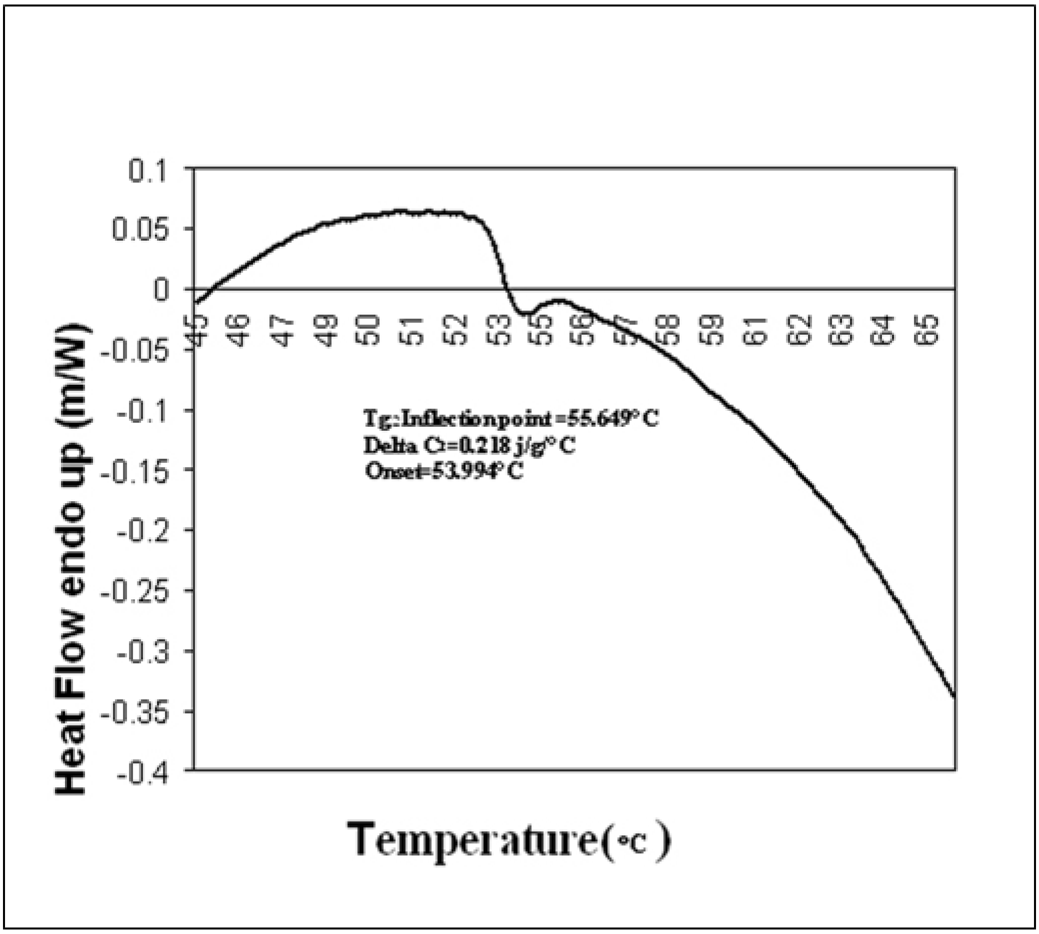

Figure 2: DSC Thermogram of rice sample extruded at 150°C and 11”%

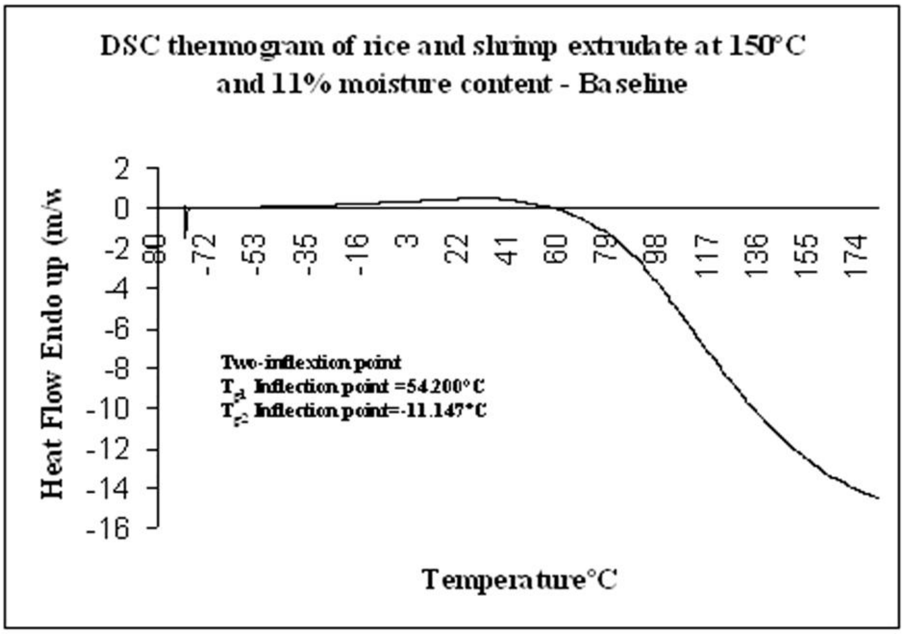

Fig. 3: DSC thermogram of rice shrimp extrudate 150ºC and 11% moisture content- Baseline

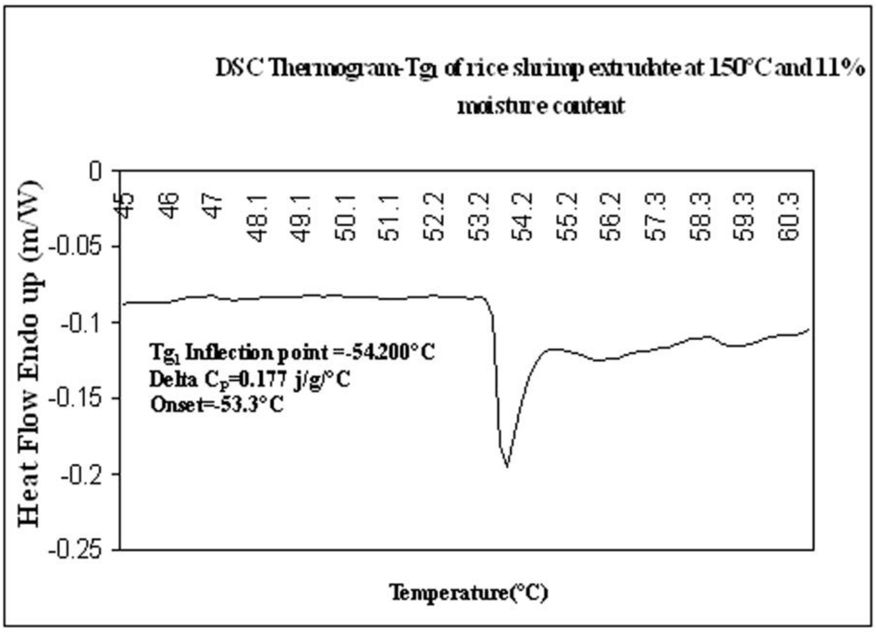

Figure 4: T_{g1} of rice shrimp extrudate at 150ºC and 11% moisture content

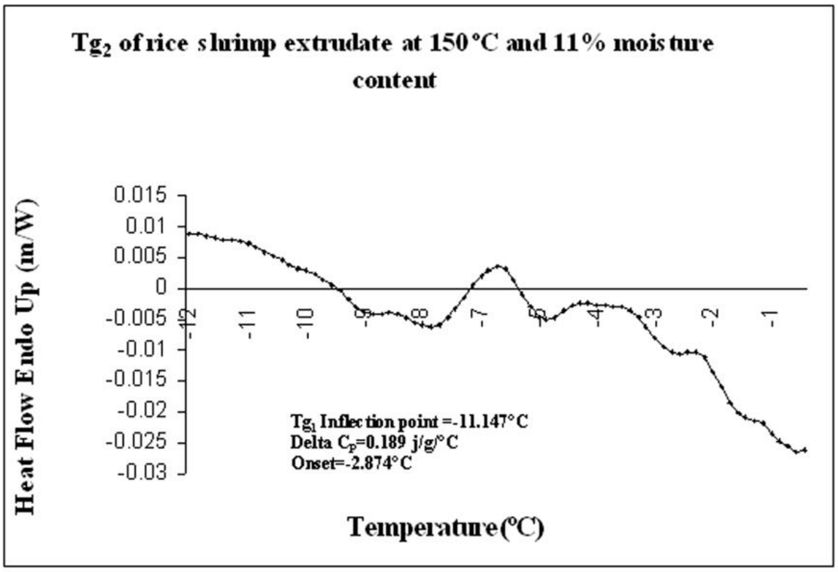

Fig. 5: T_{g2} of rice shrimp extrudate at 150ºC and 11% moisture content

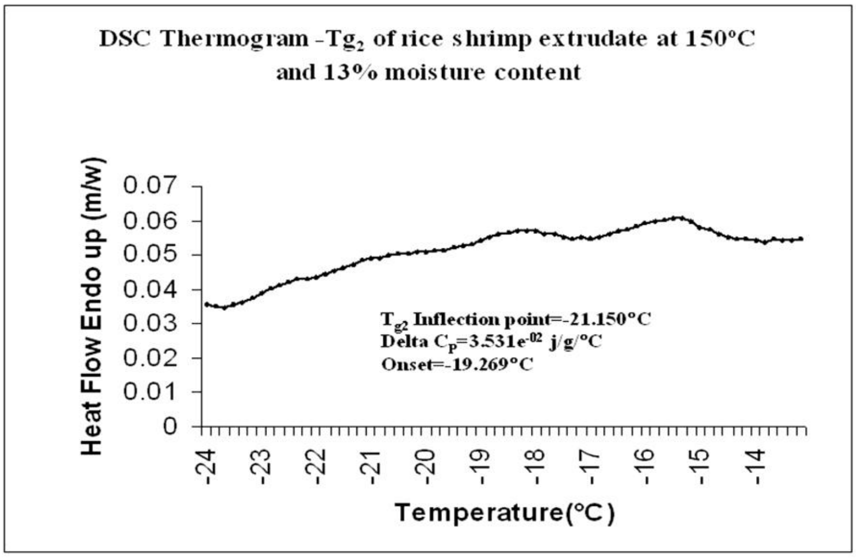

Figure 6: T_{g2} of rice shrimp extrudate at 150ºC and 13% moisture content

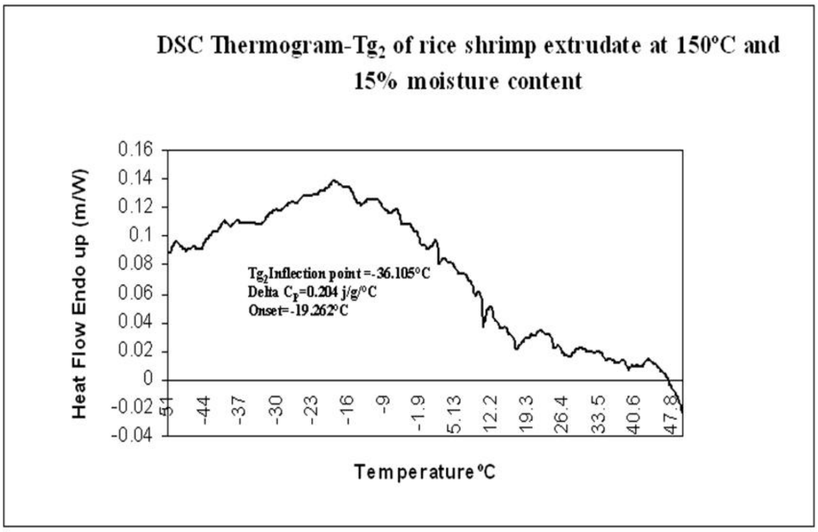

Figure 7: T_{g2} of rice shrimp extrudate at 150ºC and 15% moisture content

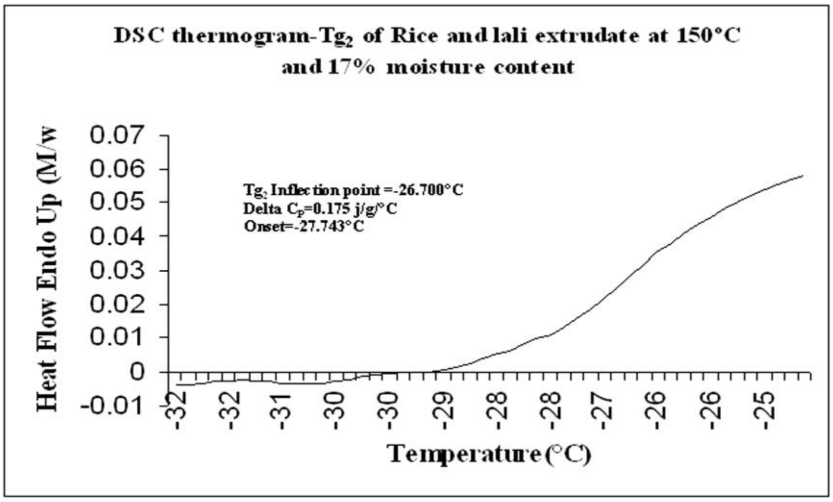

Fig. 8: T_{g2} of rice shrimp extrudate at 150ºC and 15% moisture content

Sl.no	**Temperature °C X_1**	**Moisture % X_2**	**Shear force (N) Y_2^c**
1	130	11	24.41± 0.168
2	150	13	15.76 ±0.144
3	110	11	28.82 ±0.44
4	150	11	19.10 ±0.240
5	110	13	25.55 ±0.266
6	150	17	14.52 ±0.489
7	130	15	19.74±0.72
8	130	17	18.22±0.221
9	170	15	14.52 ±0.168
10	150	15	14.12±0.44
11	170	17	16.12±0.115
12	130	13	22.56±0.104
13	110	15	20.13±0.165
14	170	11	18.89±0.76
15	110	17	18.56±0.45
16	170	13	15.56±0.67

Table-1: Result of the effect of process temperature and moisture on shear force