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Rheological determination of thermally treated Water clover leaves puree

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Abstract- **Rheological behavior of water clover (Marsilea vestita) leave puree is important for the design and establishment of processing units. All rheological measurements were carried out in the temperature range of 28-60ºC. The Power law fit with yield stress provided a good description of the flow behavior of the puree and behaved as a shear thinning fluid. The storage modulus (G') exhibited larger than the loss modulus (G'') for the puree under oscillatory shear tests. Puree showed decrement in the consistency index from 337.65±0.94 to 189.24±0.67 significantly (p<0.05) with the increment in the temperature level.**

Key words: **Power law, Rheology, Water clover leaves.**

I. INTRODUCTION

Marsileaceae is a family of rooted amphibious ferns having ability to live both in aquatic and terrestrial environments [1]. In this family, there were three subdivision namely Marsilea, Regnellidium and Pilularia among which marsilea ought to be in a cosmopolitan genus of 50-80 species [2]-[5]. Water clover (Marsilea vestita) leaves were found in shallow water on bottom rich in clay and silt. It forms a more or less monospecies communities [6] and rooted in the bottom of clayey soil in submerged water [7]. The small leaves of size approximately 2.3 mm of average length are capable of converting submerged leaf forms to a land form of darkness and also useful for photomorphogenetic studies [8]. The leaves were eaten by various tribal communities of Anamailais hills,Western Ghats, Coimbatore district, Tamil Nadu [9]. Marsilea vestita leaves were found to have medicinal uses during cough, bronchitis, diabetes, eye diseases, skin diseases etc [10].

Fresh leaves being decomposable need to be taken care of, so as to retain their freshness processing/preservation are required or else micro-organisms are liable to grow in due course of time leading to obnoxious smell. Conversion of water clover leaves into puree form could retain color and flavor in a semi-solid way having qualities close to the fresh ones. Recently, the market of various puree/paste has increased manifold due to their demand in the fast food industries. Conversion of vegetable into puree exhibits thermal treatment as well as disposition of the tissues. Purees are considered as intermission of soft particles in a viscous serum or gel [11]. In food products, rheology helps in the determination of parameters which can be correlated with other quality attributes [12]. In order to have better quality of food products it is very important to know the rheological properties. Measurement or prediction of the rheological properties of foods is very important in the design operation and optimization of processes as well as the control of quality of food products. The dynamic rheological properties, storage modulus (G') and loss modulus (G") were the important parameters used for the determination of the viscoelastic behavior of the samples during thermal treatment [13]. Some factors are there which are in responsible for the deterioration of the rheological behavior of pureed foods such as temperature [14], [15], total soluble solids [16], [17], particle size, shape and distribution [18], [19] and may also depend on the rate of shear or shear stress [20].

In the present work, an attempt has been made to study the rheological properties of blanched and unblanched puree at temperature ranges from 28 to 60 ºC. The storage modulus, loss modulus, flow behavior of the puree and FTIR analysis have also been evaluated.

EXPERIMENTAL PROCEDURE

Water clover leaves were obtained from the local market of Raipur, in the state of Chhattisgarh. The leaves were washed with normal tap water for 2-3 times to remove some unwanted particles present on it and drained. Afterwards the leaves were dried in room temperature for 30 mins.

2.1 Preparation of puree (blanched and unblanched)

Water clover leaves were blanched for 3 min in hot water (85 ºC). Blanching aimed to inactivate the enzymes responsible for senesce and bad smell [21]. The blanched leaves were immediately cooled by adding chilled water and the excess water was drained. The blanched puree was comminuted in wet grinder. The comminuted puree was sieved (14 mesh aperture size). The puree was stored in deep freezer (-7 °C) until further use. The pH and TSS (total soluble solid) of the puree was measured using pH meter and refractometer. Adjustment of pH was done using buffered solution by combining 0.1 M citric acid with 0.2 M disodium hydrogen phosphate (Mcllvaine's buffer) to the desired pH ±0.05 [22].

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For unblanched puree, the fresh leaves were converted into puree as described earlier without blanching.

2.2Rheological measurement

The rheological analyses of water clover leaves puree was performed on the MCR-52 Rheometer (Anton Paar GmbH, Austria). Puree was placed in a 1 mm gap setting using parallel plate geometry of 25 mm diameter (pp 25) and selection of plate was done according to thumb rule. The dynamic viscoelastic functions of blanched and unblanched puree were measured in terms of storage modulus (elastic modulus) G' and loss modulus (viscous modulus) G" at four different temperature range (28º, 40º, 50º and 60 ºC). Fresh samples were used for each experimental run to avoid the effects of aging to prevent from high shear rate during sample loading, Proper care was taken. Strain sweep test and frequency sweep test were carried out at above mentioned temperatures. Strain sweep tests were performed at constant frequency of 1 Hz to determine the limit of linear viscoelastic regime of the sample (LVR) and frequency sweep tests were carried out at constant strain of 0.08% in the range (I to 30 Hz) frequency in the field of LVR at above stated temperatures. The data of rheological measurements were analyzed using the RheoPlus software of Anton Paar GmbH. All the rheological measurements were performrd by the method described as in [23].

2.3 Fourier transform infrared spectroscopy (FTIR)

After the preparation of puree of blanched and unblanched it was allowed to centrifuge using 80% acetone as an extractant. The supernatant extract obtained after centrifuging the puree was further used for FTIR analysis. FTIR spectra of blanched and unblanched sample were recorded on KBr Press (M-15) by technosearch intruments. For each measurement, a total of 32 scans were collected at 4 cm^{-1} resolution. The samples were measured at wave numbers ranging from 4000 to 500 cm^{-1} through FTIR spectra and the spectral curve were obtained using Bruker software solution.

2.4 Statistical Analysis

Data were expressed as means ± standard deviation (SD) of three determinations using Microsoft Excel software. The significance difference was defined at $p<0.05$ with 95% level of confidence.

RESULTS AND DISCUSSION

3.1 Rheological characteristics

3.1.1 Frequency sweep test

Frequency sweep test were performed for blanched and unblanched puree at various temperatures (28º, 40º, 50º and 60 ºC). Two physicochemical properties (pH and TSS) of the puree were calculated before starting the experiments as this information play an important role for the growth of the plants and they were found to be 6.6 and 3.8 brix. Both storage modulus (elastic modulus) G' and loss modulus (viscous modulus) G" for unblanched and blanched puree were found to increase with increase in the temperature (Fig. 1 and 2) however the loss modulus G" show small damping with frequency and the degree of overshoot and damping, increases with increasing temperature. Storage modulus G' also exhibited damping but not as much as G". The G' of the puree sample were found higher as compared to G" and hence exhibit a prevailing solid like behavior. The highest G' values throughout the frequency range were observed at 60 ºC for blanched leaf puree. On increasing the temperature, value of G' also increases for both blanched and unblanched samples; however, this is contradicting. Blanched sample processed at 28 ºC were found to have 2-fold lower G' to the unblanched sample. "Reference [13] studied the rheological characteristics of date paste over the temperature range of 20 to 80 ºC. The values of the storage modulus (G') were found to be much higher than the loss modulus (G") at frequency ranges from 0.1 to 10 Hz and date paste showed the weak gel behavior based on the mechanical spectra". A similar behavior has been reported for rocket leave puree as in [24] over the temperature ranges of 25 to 70 ºC. All the puree samples (with and without stem) exhibited an elastic modulus (G') larger than the loss modulus (G") in the tested frequency range and the value of G' increased with temperature.

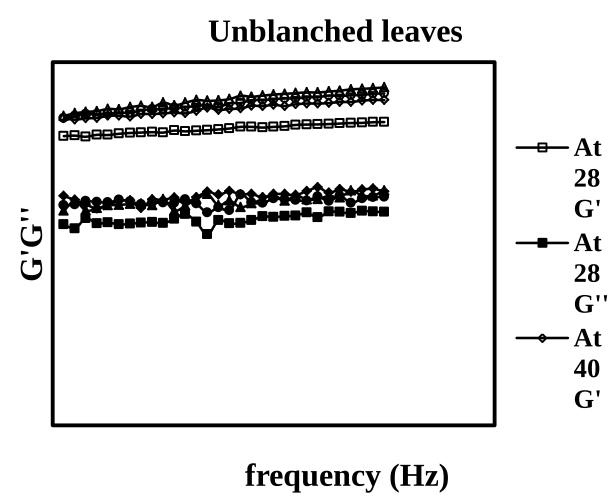

Fig. 1 Frequency sweep tests for unblanched puree at a constant strain of 0.08%

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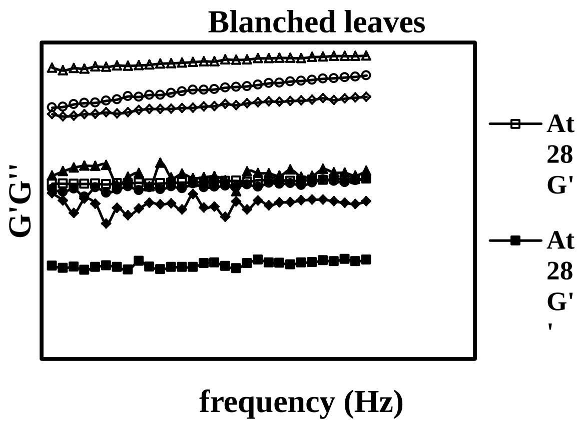

Fig. 2 Frequency sweep tests for blanched puree at a constant strain of 0.08%

3.1.2 Steady shear rheology of blanched sample

Shear stress (τ)-shear rate (γ) curves for blanched puree sample at various temperatures is illustrated in Fig. 3. The shear stress of puree decreased with the increase of temperature. The flow behavior of the puree sample was well described by power law fit and the parameters were illustrated in Table 1.

$$\tau = k\gamma^{n} \quad (1)$$

where τ is the shear stress (Pa), *K* is the consistency index (Pa s^n), *n* is the flow behavior index and *γ* is the shear rate (s^{-1}). *K* value of puree decreases from 337.647 to 189.237 significantly ($p<0.05$) as temperature was raised from 28 to 60 °C. Puree exhibit power law fit with yield stress and τ_o was found to decrease with increase in temperature. The experimental data obeys power law fit after the yield is overcomes and hence for the point shown in the figure, the references has been made to power law fit, though overall data is certain to be Hershel Bulkley model. τ_o values were found to be 310, 280, 210 and 150 that is higher ($p<0.05$) in samples as temperature was raised from 28 to 60 °C. *n*<1 refer to shear thinning behavior. In the present work *n* was found to vary from 0.177 to 0.204. The reason of shear thinning behavior is due to complicated interaction of the particles in dispersion with each other. The model equation obtained by using the coefficients given in Table 1 was presented by a solid line in Fig. 3 and it was observed that good fit of model was obtained that certain that the behavior is power law (R^2 for temperature 28, 40, 50 and 60 °C was obtained as 0.982, 0.977, 0.924 and 0.932 respectively, using ANOVA analysis). The steady shear viscosity (*η*) is presented as a function of shear rate at various temperatures in Fig. 4. The puree exhibited shear thinning behavior and at all the temperature range, viscosity decreases as shear rate increases ($p<0.05$). The rheological characteristics of coriander leaf puree were studied at temperatures (50-80 ºC) [25]. The puree showed pseudoplastic behavior with the flow behavior index (*n*) within the range of 0.61 and 0.7 which was well described by Herschel-Bulkley model. Similar behavior was optimizing in the rheological characteristics and color changes of ginger paste over the temperature range of 20-80 ºC [20]. Ginger paste exhibited pseudoplastic in nature and the flow behavior was defined by Herschel-Bulkley model. On increasing the temperature, both consistency index (*K*) and apparent viscosity decreased and the flow behavior index (*n*) was found to be in the range of 0.66 to 0.82. "Reference [26], studied the rheological behavior of coriander and mint leaf puree at temperatures (30 to 80 ºC). Both the puree showed non-Newtonian flow behavior described by Herschel-Bulkley model and the consistency index (*K*) of both the leaf puree was well described by the Arrhenius model". For various purees, similar observations have been reported by other researchers [27], [28].

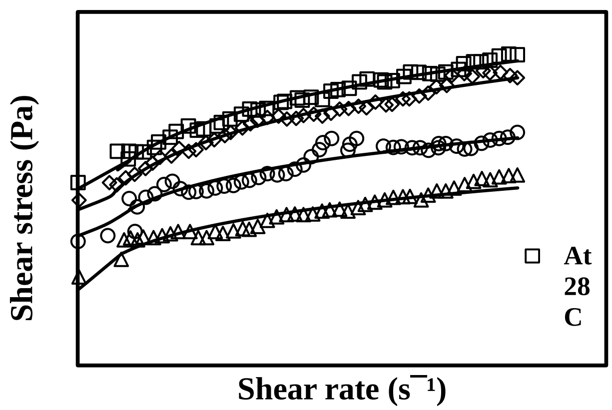

Fig. 3 Steady flow behavior of water clover leave puree (blanched) at selected temperatures

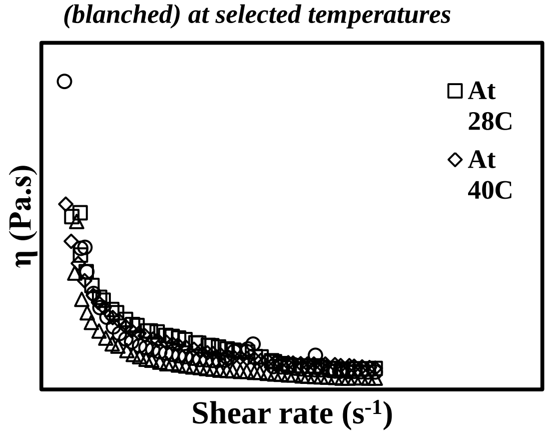

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Fig. 4 Influence of temperature on steady shear viscosity of blanched water clover leaves puree

Table 1: Power Law Model Parameter for Marsilea Vestita Leave Puree (Blanched)

Temperature (°C)	Consistency index, *K* (Pa.s^n)	Flow behavior (*n*)	R^2
28	337.65±0.94[b]	0.185±0.02[b]	0.982
40	305.21±1.64[a]	0.204±0.032[a]	0.977
50	256.98±0.57[b]	0.177±0.03[b]	0.924
60	189.24±0.67[b]	0.202±0.028[b]	0.932

*Values (mean ± standard deviation, *n*=3) in the same column followed by different letters are significantly different ($p<0.05$).

3.2 FTIR analysis

FTIR spectroscopy was employed to explore the changes in functional groups induced by preparation process. It is a sensitive technique for identifying organic/inorganic chemicals in a whole range of applications. FTIR spectra of the unblanched and blanched puree sample are presented (Fig. 5) in which the upper curve signifies the behavior of blanched sample whereas lower spectra are for unblanched sample. For both the samples the stretching vibrations of (C=O) at 1660-1710 cm^{-1} and (OH, H-bonded) at 3200-3500 cm^{-1} were observed. Functional group obtained during analysis of the sample signifies the presence of ketone and alcohol group. No such differences of functional groups were found in blanched as well as unblanched puree samples. Similarly, FTIR spectra of the Aloe vera suspension in the polysaccharides region of (1200-800 cm^{-1}) were reported in [29]. In the region of (1200-1000 cm^{-1}) on increasing the absorption, stretching vibrations of (C-OH) group and (C-O-C) bond were observed.

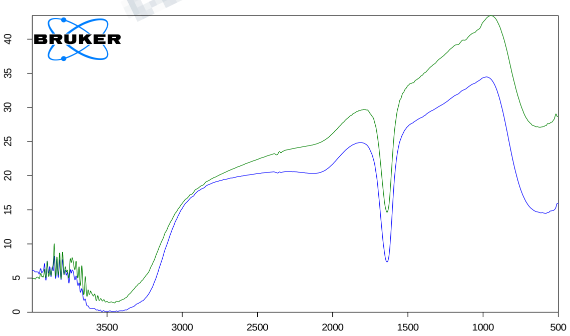

Fig. 5 FTIR spectra of blanched and unblanched puree

CONCLUSION

The flow behavior of water clover (Marsilea vestita) leave puree exhibited shear thinning behavior (pseudoplastic) with the flow behavior index (n) in the range of 0.177-0.204 and the rheological characteristics was adequately defined by the Power law fit with yield stress. At a constant strain of 0.08%, as temperature increases the frequency sweep tests for both unblanched and blanched puree sample was found higher G' values as compared to G" values. The presence of functional group can be observed using FTIR data and this data could be helpful in the researchers working in the field of food science to understand the nature of the puree and also correlate to the chemistry behind the effect of heat on the purees.

NOMENCLATURE

G' = storage modulus
G" = loss modulus
τ = shear stress (Pa)
γ = shear rate (s^{-1})
η = viscosity (Pa s)
n = flow behavior index
k = consistency index (Pa s^n)
R^2 = Regression coefficient
M = molarity

ABBREVIATIONS

FTIR = Fourier transform infrared spectroscopy
KBr = Potassium bromide
LVR = linear viscoelastic regime
TSS = Total soluble solids
SD = Standard deviation

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