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Glass Transition Kinetics and Fragility of Amorphous Biopolymers

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Abstract: **Angell proposed the concept of Fragility and it is extensively used to categorize the strong to fragile properties of glass forming liquids. In our present work, we report the fragility index m, of Papain. Differential Scanning Calorimetric (DSC) measurements at various heating rates in the range 5 to 20 K/min are utilized to determine glass transition temperatures (Tg). The Tg values are taken from elsewhere. Three theoretical models, Vogel-Fulcher-Tammann (VFT), Lasocka and Moynihan are employed to determine fragility index, m. The average value of fragility index, m, for the amorphous biopolymers Papain from three methods isfound to be 32 and it indicates strong fragile material according to Angell`s theoretical approach.**

Index Terms: **Biopolymer, Glass Transition (T_g), Activation Energy for Glass transition (E_g), Fragility index.**

I. INTRODUCTION

Papain is a proteolytic enzyme extracted from the raw fruit of the papaya plant. This is procured by cutting the skin of the unripe papaya (Ezekiel A., et al.,2012). Papain is a single chain protein with the molecular weight of 23.406 x103 daltons. It contains 212 amino acids with four disulfide bridges (Drenth, J., et al.,2012). Papain enzyme has high decomposing ability and biological activity so is widely used to treat ulcers. It is also used in detergents, textiles and meat industry. Owing to the good therapeutic property, Papain is also used as potential drug for bacterial and fungal diseases (Sainan S., et al.,2008).

The concept of fragility is originally introduced by Angell (Angell C., et al.,1985). According to his concept, glass forming liquids are classified into three categories. The first category is strong glass formers, which obey an Arrhenian behaviour in the Angell plot and the second category is fragile glass formers and are viscosity dependent. These are studied by Vogel-Fulcher-Tammann (VFT) relation and the third category are intermediate glass formers and lie between the first and the second categories (Angell C., et al.,1995). The fragility graphs are generally evaluated using viscosity data. However, Tg dependent on heating rate, measured by differential scanning calorimetry (DSC) can also be adequately exploited to understand the fragility (Bruning, R., et al.,1992).

Many synthetic polymers exhibit high fragility and deviate from most of the behavior known for metallic and non-polymeric glass forming glasses. Fragility of synthetic polymers are studied extensively, whereas the study of biopolymers is scarce in the literature. The main purpose of the present work is to understand the fragile nature of these biopolymers to utilize in the food industry.

II. EXPERIMENTAL METHODS

The DSC of the biopolymer Papain recorded in the nitrogen atmosphere at different heating rates5, 10, 15 and 20 K/min in the temperature range 30 to 450 ^{0}C. The glass transition temperatures, T_g data to calculate fragility index, m, were taken from elsewhere (Muthulakshmi, S., (2013).

III. RESULTS AND DISCUSSION

Three different methods are utilized to determine the fragility parameter, m and these are enumerated below. VFT fitting method

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The dependence of the T_g with β in DSC scans is given in terms of VFT equation (Vogel H., 1921; Fulcher G.1925).

$$\beta T_g = Ce^{(B/(T_0 - T_g))} \tag{1}$$

Here C, B and T_0 are adjustable VFT parameters and T_0 is called Vogel temperature or the ideal glass transition temperature. This is generally approximated to the asymptotic value of T_g , at the limit of infinitely slow cooling rate. C has the dimensions of heating rate and B = D T_0, where D is called the strength parameter. The Equation 1 is written as

$$\ln \beta T_g = \ln C - B/(T_g - T_0) \tag{2}$$

The fragility index m at a particular T_g can be calculated from the Equation 3, (Tammann, G., et al.,1925).

$$m = (BT_g/2.303(T_g - T_0)^2 \tag{3}$$

From Equation 3, the value of m depends on the value of T_g. Inserting T_g and adjusting T_0 value (by checking maximum regression value), plotting ln β versus 1/ ($T_g - T_0$) , the slope B= 598.61 is determined (figure.1). Hence, substituting the B value in Equation 3, the fragility index m is calculated (Table.1). The T_0 = 400 K for the proper VFT fit is obtained.

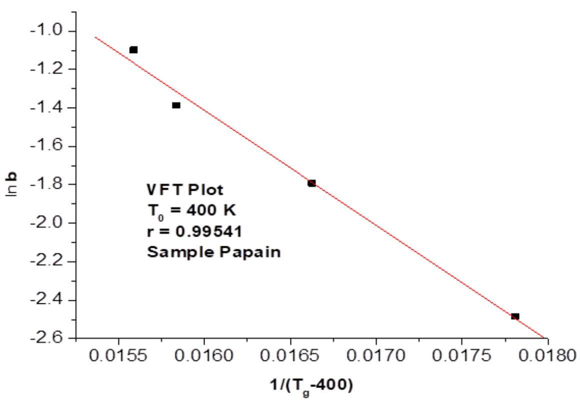

Fig. 1. Plot of VFT

A. Lasocka's method

The glass transition, T_g as a function of heating rate, β is given by Lasocka's empirical relation (Lasocka, T., et al.,1993).

$$T_g = A + E \ln \beta \tag{4}$$

Where A and E are empirical constants. Extrapolating the data to β = 1 K/min, it is possible to obtain a tentative value A = T_0, which may be the lower limit of T_g (Money, B., et al.,2009) . Plotting T_g against ln β, the value A = T_0 = 446.58 K is obtained (figure.2). Inserting this value in Equation 2, the slope B = 27.30 is obtained and substituting this B value in Equation 3, the m values are determined. The m values are tabulated for the Papain in the Table 1.

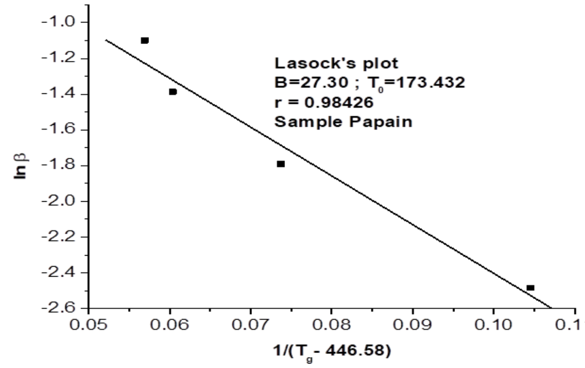

Fig. 2. Plot of Lasocka

B. Ozawa method

The fragility index, m is also calculated using the relation ([Ozawa, T., 1965).

$$m = E_g/(RT_g \ln 10) \tag{5}$$

Where E_g is the activation energy of glass transition and R is universal gas constant. Besides the Kissinger equation, another widely utilized non-isothermal method is the so-called Ozawa equation which can be expressed as

$$\ln \beta = -1.0516\, E_g/RT_g + constant \tag{6}$$

Where β and E_g are the heating rate and activation energy of glass transition, respectively. A plot of ln β against 1000/T_g (Figure.3) yields an approximate straight line with a slope of -1.0516E_g/R. From the slope, E_g = 278.76 kJ/mol is obtained and substituting in Equation 5, m values are determined (Table 1).

Fig.4 shows the variation of m with the heating rate. m = 30 is the fragility index for the studied sample at 10 K/min (intersecting point). The value m = 30 indicates from the Angell's scheme, Papain falls under a strong fragile glass.

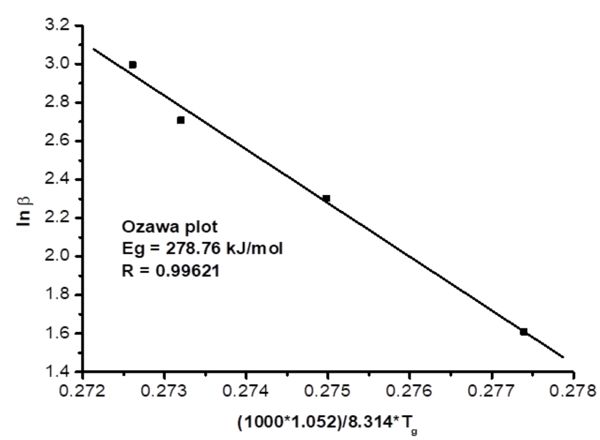

Fig. 3. Plot of ln β versus (1000* 1.052) / T_g

Table I. Fragility parameter, m for Papain from different methods

Heating rate (β) K/min	T_g (K)	Fragility		
		VFT	Lasocka	Ozawa
5	456.15	37.61	59.07	31.92
10	**460.15**	**33.06**	**29.63**	**31.64**
15	463.15	30.19	20.00	31.43
20	464.15	29.32	17.83	31.37

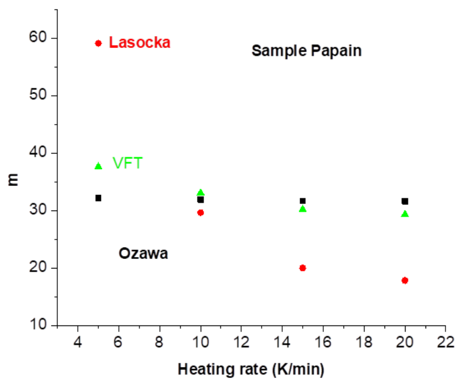

Fig. 4. Plot of m versus heating rate (K/min)

CONCLUSION

The thermal stability of biopolymer Papain has been evaluated in terms of fragility parameter (m) using three different methods based on the glass transition temperature (T_g) determined from DSC runs. Table 1 shows the consistency of m values determined from three different approaches namely, VFT, Lasocka and Ozawa. The fragility parameter, m is around 30 and this reflects from the figure.4 for the heating rate 10 K/min. It is also consistent from the three methods. The Fragility, m = 30 indicates from the Angell's approach, the biopolymer Papain behaves like a strong fragile glass. To corroborate this behavior, the study of fragility for different biopolymers is in the pipeline.

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