Journal of Physics: Conference Series 249 (2010) 012050

Effect of PET on the crystallization of lithium/sodium acetate glasses studied by isothermal and non-isothermal kinetic methods

Silvanio S L da Costa¹, Marcelo L dos Santos¹, Marcelo A N Beltrao¹, Charlene R S Matos¹, Ana C S Alcantara¹, Iara F. Gimenez¹, Oswaldo L Alves², Ledjane S Barreto¹

¹Universidade Federal de Sergipe, DQI (Department of Chemistry), ²LQES (Solid State Chemistry Laboratory), IQ (Institute of Chemistry), UNICAMP

ledjane@ufs.br

Abstract. The kinetic parameters for the crystallization of CH₃COOLi/CH₃COONa glasses varying the Li:Na mole fraction LN21(2:1), LN31(3:1), LN41(4:1) and LN32(3:2) have been evaluated by isothermal and non-isothermal DSC measurements. Crystallization of LN21 samples containing variable amounts of poly(ethylene-terephthalate) (PET) has also been studied. Values of the Avrami exponent *n* varying between 2.05 and 2.33 were obtained from both isothermal and non-isothermal methods for all LN glasses, indicating a diffusion-controlled crystal growth with a decreasing nucleation rate. The more pronounced effect of PET on glass crystallization has been observed for low polymer amounts, being interpreted as due to polymer miscibility with the glass, which is absent for high PET amounts. The value of n = 4.75 for LN21+PET (3%) suggests a change in the crystallization energy (*E*) decreased with increasing PET amount, evidencing an improvement in glass stability against crystallization.

1. Introduction

Acetate glasses can be prepared by melting alkali metal acetates at relatively low temperatures [1-3]. Duffy and co-workers have shown that the structures of the resulting ionic glasses are comprised by M^+ and $C_2H_3O_2^-$ entities, the last one with two oxygen atoms able to coordinate metal ions [4,5]. To further understand the glass structure, we reported a computational study of structural and dynamic properties of crystalline and molten alkali acetates from molecular dynamics simulations [6-8]. We found that the crystalline phases are formed by layers of acetate anions and alkali cations and the structure of glassy phases can be described by the formation of deffects and expansion of the system, as a result of increasing thermal vibrations with heating. Glebovsky and co-workers described the structure of the first coordination sphere around lithium cations in glassy acetates by quantum chemical calculations [9].

Owing to their optical transparency (240 - 1400 nm) and the low melting temperatures, carboxylate glasses have been studied as hosts for luminescent species such as Eu(fod)₃Phen-NO [10]. These glasses can also be useful as hosts for controlled release of pharmaceutical, biocidal, fungicidal, or hormonal species [11,12]. However, a major drawback to practical applications of these glasses is the

high hygroscopicity, a common feature of many crystalline acetates of alkali and alkali earth elements. An alternative to improve the durability is the incorporation of polymeric additives to the glass composition. Important properties such as the optical transparency can be preserved by the proper choice of polymer, which must be thermally stable at the glass melting temperature.

Here we report a thermal analysis study of mixed Li/Na acetate glasses in the presence of poly(ethylene terephthalate) (PET) by isothermal and non-isothermal data. Empirical methods [13-15] have been used for determination of kinetic crystallization parameters.

2. Experimental

2.1. Materials

Anhydrous lithium acetate was obtained by the reaction of acetic acid and lithium carbonate. The final product was dissolved in water, filtered to eliminate residues, and recrystallized as the hydrated salt. The anhydrous phase was obtained by heating the corresponding hydrate under vacuum at 120 °C for 8 h. Reagent grade sodium acetate was purchased from Merck. Granular PET (poly(ethylene terephtalate)) was purchased from Aldrich.

2.2. Preparation and characterization of samples

The DSC measurements were carried out using aluminum cells under N₂ at 50 mL/min in a TA 2010 instrument, which was calibrated periodically using In and sapphire as standards. Glass samples were prepared by melting *in situ* mixtures of the raw materials of about 12 mg were in the DSC cell, followed by cooling with liquid nitrogen. Afterwards the isothermal and nonisothermal studies were carried out by reheating the freshly formed glass samples. Heating rates of 10, 12.5, 15, 17.5 and 20 °C/min were used for the non-isothermal study. The temperatures for isothermal studies were 109, 119 and 129 °C, and in this case the samples were heated to the chosen temperature and kept at this condition for 120 min. The samples were denoted LN41 (80:20 Li:Na mol%), LN31 (75:25 Li:Na mol%), LN21 (66:33 Li:Na mol%), LN32 (60:40 Li:Na mol%); LiAc (100 mol%). For the study of PET effect, the glass composition LN21 was chosen and, according to the polymer content (mass %), the sample nomenclature is as follows: LN21+PET (3%), and LN21+PET (30%).

For the measurements of optical microscopy images, a portion of the mixed raw materials was heated at 10 °C/min over glass plates in a Leica DMLM optical microscope coupled to a Metler Toledo FP90 heating accessory up to the melting temperature. Images were recorded at each 5 °C with a 20X magnifying lens.

3. Theory

Thermal analysis (TA) methods such as DTA or DSC are widely used for kinetic analysis of crystallization processes in amorphous solids. The crystallization kinetics based on these data is usually interpreted in terms of the standard nucleation-growth model formulated by Kolmogorov-Johnson-Mehl-Avrami [16-18]. All the theory can be found in references from [19-23].

This model describes the time dependence of the fractional crystallization x, usually written in the following form [19]

$x = 1 - \exp\left[-(kt)^n\right]$

(1)

where x is the volume fraction crystallized isothermally; t is the time and k is a constant while n is referred to as the Avrami exponent, a dimensionless parameter related to the morphology of the crystal growth. For the analysis of isothermal data, an equivalent expression of Eq. (1) can be used as follows [20]

 $\ln [-\ln(1-x)] = n \ln k + n \ln t$ (2) it follows from this expression that a plot of ln [-ln (1-x)] versus ln t gives n from the slope and k is calculated from the intercept. The crystallization activation energy E is obtained from the equation $\ln k = \ln k_{\theta} - E/RT$ (3) Journal of Physics: Conference Series 249 (2010) 012050

(4)

doi:10.1088/1742-6596/249/1/012050

where k_0 is the frequency factor (s⁻¹), *E* is the apparent activation energy (kJ/mol) representing the kinetic barrier to crystallization, and *T* is the temperature by plotting ln *k* as a function of 1/*T* for different temperatures.

The Avrami exponent *n* may also be obtained through non-isothermal measurements using the pseudo-isotherm method introduced by Ozawa [21]. In the non-isothermal method the sample is heated at a constant rate (α), and the heat flow is recorded as a function of temperature or time and the following expression can be used:

$\ln \left[-\ln \left(1 - x \right) \right] = n \ln \left[k \left(T - T_0 \right) \right] - \ln \alpha$

where x is the fraction crystallized at temperature T with heating rate α .

In a non-isothermal DSC experiment, the sample temperature is increased linearly versus time *t*. The heating rate is α (=dT/dt) and the temperature is expressed as $T = T_0 + \alpha t$, where T_0 is the initial temperature. In these conditions the rate constant, *k*, changes continually versus time and Eq. (1) must be written as follows [20]:

$$\left|-\ln(1-x)\right|^{1/n} = \int_0^t k(T(t'))dt'.$$
(5)

Solving this relation leads to the following equations [15]:

$$\frac{1}{n}\ln(-\ln(1-x)) = \ln\frac{k_0R}{E} + \ln\frac{T^2}{\alpha} - \frac{E}{RT},$$
(6)

$$\frac{1}{n}\ln(-\ln(1-x)) = \ln\frac{k_0E}{\alpha R} - 2\ln\frac{E}{RT} - \frac{E}{RT}.$$
(7)

Consequently one may draw straight lines from which the value of E/R is deduced. Typical plots are those suggested by Ozawa [19]

$$\left|\frac{d(\ln\alpha)}{d(l/T_p)}\right|_x = -\frac{E}{R},\tag{8}$$

and Chen [22]

$$\left|\frac{d\left(\ln T_{p}^{2}/\alpha\right)}{d\left(l/T_{p}\right)}\right|_{x} = -\frac{E}{R}.$$
(9)

The apparent activation energy has been calculated also from the constant fraction method (CFM) [23] using the equation:

 $\ln(t_x) = const - \ln A + E/R (1/T), \tag{10}$

where t_x is the time for a transformed fraction for isothermal experiments, *R* is the gas constant, and *A* is a constant.

4. Results and discussion

Information related to nucleation and crystallization mechanisms for the LN glasses with different compositions as well as the LN21 composition with different PET contents were evaluated by the determination of the Avrami exponent (*n*), from both isothermal and non-isothermal methods applied to DSC data. The DSC curves in figure 1 ilustrate typical thermal profiles of the LN21 glass in the absence and in the presence of PET where the glass transition, crystallization and melting can be observed. In this work we report only the addition of PET to the LN21 composition because for the other compositions the presence of PET induced crystallization of the samples. It is worth mentioning that the DSC curves (not shown) were measured for all samples without PET, being very similar to the LN21curve.

IOP Publishing

Journal of Physics: Conference Series 249 (2010) 012050

doi:10.1088/1742-6596/249/1/012050



Figure 1- Differential scanning calorimetry curves (DSC): (a) LN21; (b) LN21+PET (3%); and (c) LN21+PET (30%).





Figure 2- Plot of $[-\ln (1-x)]$ versus ln t for determination of of Avrami exponent from isothermal method for LN21+PET (3%) (a) and for LN21+PET (30%) (b).

Figure 3- Plot of [-ln (1-x)] versus ln α for determination of of Avrami exponent from isothermal method for LN21+PET (3%) (a) and for LN21+PET (30%) (b).

For the determination of Avrami exponent, typical illustrative plots of $\ln[-\ln (1-x)]$ versus $\ln t$ from isothermal data and $\ln[-\ln (1-x)]$ versus $\ln \alpha$ from non-isothermal methods are shown in figures 2 and 3. Similar plots (not shown) were obtained for all samples, with the resulting values of Avrami index *n* shown in table I. As expected, both plots resulted in straight lines. Table I gives the values of Avrami exponent *n* determined in this study from both methods, along with the ranges for the values of *n* presented in the literature [24] for interface-controlled processes and diffusion-controlled processes.

Table 1- values of the Avram exponent for different samples and meaning of the values							
Composition	n (Avrami)	n (Ozawa)	Transformation Condition (n)				
LN41	2.33±0.06	1.99±0.31	DCG	ICG			
LN31	2.11±0.06	1.85±0.26	^a >2.5	^a > 4			
LN21	2.05 ± 0.04	2.09±0.70	^b 2.5	^b 4			
LN32	2.16±0.07	1.86±0.40	°1.5 <n< 2.5<="" td=""><td>$^{c}3 < n < 4$</td></n<>	$^{c}3 < n < 4$			
LiAc	2.24±0.07	2.17±0.52	°1.5	"3			
LN21+PET(3%)	3.13 ± 0.01	4.75±0.25					
LN21+PET(30%)	2.16 ± 0.06	2.98 ± 0.55					

Table I- Values of the Avrami exponent for different samples and meaning of the values

DCG – Diffusion-Controlled Growth, ICG – Interface-Controlled Growth, ^a Increasing nucleation rate, ^b Constant nucleation rate, ^c Decreasing nucleation rate, ^d Zero nucleation rate. *Source*: Reference [24]

In the absence of PET the results show a reasonable agreement between isothermal and nonisothermal studies. This finding suggests that the assumptions made for the extension to nonisothermal experiments of Avrami's equations can be considered acceptable. The values obtained indicate that the crystallization mechanism is barely sensitive to the sodium amount since the values obtained for the Avrami exponent were in the range 2.05-2.33 from isothermal method and 1.85-2.09 from nonisothermal method. Values in this range suggest a crystallization mechanism for the different LN glass compositions controlled by diffusion with a decreasing nucleation rate.

The values of the Avrami exponent for the LN21 glass composition increased in the presence of PET, which in general suggests a changing from diffusion-controlled to interface-controlled crystal growth. For the sample containing only 3 % of PET, the value of *n* from the isothermal method was 3.13 and from the non-isothermal measurement was 4.75, both relatively high in comparison to the values found for the PET-free LN21 composition. On the other hand, the values of *n* decreased with increasing PET proportion and the sample containing 30 % PET exhibited an Avrami exponent closer to that for PET-free sample, which could be related to an effect of the decreasing acetate percent. The general trend (increase in *n*) could be explained by phase segregation in the presence of PET, which is more pronounced for higher PET amounts. An examination of the melting process by optical microscopy images with *in situ* heating, figure 4, has been carried out to check for this hypothesis. The images evidenced that the LN21 glass containing 3 % PET appears homogeneous in this magnification and that for higher PET contents, the acetate glass-phase and PET apparently are segregated. Despite the low resolution compared to electron microscopy techniques, optical measurements were chosen due to the possibility of heating and forming in situ the low-melting glasses.



Figure 4- Optical microscopy images with 20X magnification obtained at increasing temperature up to melting for the compositions (a) LN21; (b) PET; (c) LN21 + PET3%; (d) LN21 + PET30%.

4.1. Determination of activation energies

The apparent activation energy for LN glasses with variable Li content and for the LN21 glass with different PET amounts have been calculated by constant fraction method (CFM) [23], figure 5. The observed behavior of the curves in (a) indicates that the activation energy decreases when the lithium concentration decreases.

Journal of Physics: Conference Series 249 (2010) 012050

doi:10.1088/1742-6596/249/1/012050



Figure 5- Variation of the activation energy with crystallized fraction for PET-free LN 31, 21 and 41 glasses (a) and for free and PET-containing LN21 glass (b).

In general the apparent activation energies (b) decrease in the presence of PET. For the evaluation of PET effect, activation energy has been determined by CFM method, also by the Arrhenius equation (3), and by the non-isothermal methods of Ozawa and Chen. Eq. (8) and Eq. (9). Typical plots are shown in figure 6 for LN21-PET 3%. All the values for apparent activation energy are summarized in table II.



Figure 6- Different plots for the determination of the apparent activation energy for the sample LN21+PET3%: (a) by constant fraction method (CFM) (b) by the Arrhenius plot; (c) by the Ozawa method; (d) by the Chen method.

Samples	$E / \text{kJ mol}^{-1}$ ln α Vs. 1/T _p	$E / \text{kJ mol}^{-1}$ ln (T _p ² / α) Vs. 1/T _p	E / kJ mol ⁻¹ (CFM)	$E / kJ mol^{-1}$ ln k Vs. 1/T
LN21	111.94 ± 24.19	104.90 ± 24.19	90.22 ± 23.79	184.75 ± 7.98
LN21+PET (3%)	86.65 ± 4.01	79.59 ± 4.03	76.85 ± 15.69	180.04 ± 7.81
LN21+PET(30%)	89.12 ± 10.12	82.04 ± 10.12	92.87 ± 19.01	173.70 ± 4.77

Table II- Apparent ac	tivation energy	from isot	thermal and	non-isothermal	methods.
11	0,				

In table II, the observed values of activation energy for glass crystallization decreased with the addition of PET, indicating that the glass stability toward crystallization increased. As stated previously by Poulain [28], the physical meaning of the activation energy of glass crystallization involves an apparent paradox. There is an empirical correlation between the activation energy of crystallization and glass stability, according to which a lower activation energy value may indicate a lower devitrification tendency [27-30], since this parameter also represents the activation energy of the viscous flow. It is not the purpose of this work to discuss this apparent paradox, but the observed results can be related to a decreased devitrification tendency with the addition of PET.

5. Conclusions

As conclusions of this work the values observed for the Avrami exponent indicated a changing in the crystallization mechanism upon addition of PET, from diffusion-controlled to a crystallization mechanism controlled by the interface. Finally the results indicated a decreasing in the apparent activation energy when increases PET composition, which could be related to an improvement of glass stability.

6. Acknowledgements

The authors are grateful to CNPq for financial support, to CNPq-PIBIC/UFS the fellowships and to Prof. G. Cardoso for the optical measurements.

7. References

- [1] Uhlmann D R and Kreidl N J 1983 Glass-Forming Systems V.1 Academic Press, New York
- [2] Blair L A. and Duffy J A 1993 Phys Chem Glasses **34** 194
- [3] Wilk Jr N R and Schreiber H D 1997 J Non-Cryst Solids 217 189
- [4] Baranova G I, Glebovsky D N, Zhuchkova T V and Panteleev I A 2001 Mol Cryst Liq Cryst 365 1595
- [5] Ingram M D, Lewis G G and Duffy J A 1972 J Phys Chem 76 1035
- [6] Wilk Jr N Rand Schreiber H D 1998 J Non-Cryst Solids 239 192
- [7] Barreto L S, Mort K A, Jackson R A and Alves O L 2000 J Phys Cond Matter 12 9389
- [8] Barreto L S, Mort K A, Jackson R A and Alves O L 2002 J Non-Cryst Solids 303 281
- [9] Barreto L S, Jackson R A and Alves O L 2002 Phys Chem Glasses **43C** 119
- [10] Panteleev I A, Bedrina M E and Glebovsky D N 2002 Glass Sci Technol **75** 402
- [11] Beltrao M A, Santos M L, Mesquita M E, Barreto L S, Costa Jr N B, Freire R O and Santos M A C 2006 J Lumin 116 132
- [12] Blair J A, Mordue A J, Duffy J A and Wardell J L 1994 J Control Release **31** 145
- [13] Blair J A and Duffy J A 1992 Phys Chem Glasses **33** 191
- [14] Taniguchi H, Yu J, Arai Y, Fu D, Yagi T and Itoh M 2008 Mater Sci Eng B 148 48
- [15] Camacho-Lopez M A, Haro-Paniatowski E, Lartundo-Rojas L, Livage J and Julien C M 2006 Mater Sci Eng B 135 88
- [16] Poulain M 1992 J Non-Cryst Solids 140 1
- [17] Avrami M 1939 J Chem Phys 7 1103
- [18] Avrami M 1940 J Chem Phys **8** 212
- [19] Avrami M 1941 J Chem Phys **9** 177

IOP Publishing

Journal of Physics: Conference Series 249 (2010) 012050

doi:10.1088/1742-6596/249/1/012050

- [20] Cheng K 1999 Mater Sci Eng B 60 194
- [21] Tomasi C, Scavini M, Speghini A, Bettinelli M and Riccardi M P 2002 J Therm Anal Cal 70 151
- [22] Ozawa T 1965 Bull Chem Soc Jpn **38** 188
- [23] Chen M S 1978 J Non-Cryst Solids 27 257
- [24] Putnis A 1995 Introduction to Mineral Sciences, Cambridge University Press, New York
- [25] Christian JW 1975 The Theory of Transformations in Metals and Alloys, Pergamon, New York
- [26] Boutarfaia A and Poulain M 1998 J Therm Anal Cal 51 851
- [27] Branda F, A. Marotta, A. Buri, J. Non-Cryst. Solids 134 (1991) 123-128.
- [28] M. Matecki, Noiret-Chiaruttini I and Lucas J 1991 J Non-Cryst Solids 127 136
- [29] Poulain M 1996 Thermochim Acta 280-281 343
- [30] Costa B J, Poulain M, Messadeq Y, Ribeiro S J L 2000 J Non-Cryst Solids 273 76
- [31] Shiryaev V S, Adam J-L, Zhang X H and Churbanov M F 2005 Solid State Sci 7 209