AIP | Conference Proceedings

Thermodynamics of glass forming polymeric melts

Prapti B. Pandya, Ashmi T. Patel, and Arun Pratap

Citation: AIP Conf. Proc. **1536**, 655 (2013); doi: 10.1063/1.4810397
View online: http://dx.doi.org/10.1063/1.4810397
View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=1536&Issue=1
Published by the AIP Publishing LLC.

Thermodynamics of Glass Forming Polymeric Melts

Prapti B. Pandya[1], Ashmi T. Patel[1], Arun Pratap[1*]

[1]*Condensed Matter Physics Laboratory, Applied Physics Department,*
Faculty of Technology Engineering, The M. S. University of Baroda, Vadodara – 390 001, India

Abstract. The temperature dependence of the Gibbs free energy difference (ΔG) between the under cooled melt and the corresponding equilibrium solid has been analyzed for two samples of glass forming polymeric melts; polyamid-6 (PA-6), polypropylene oxide (PPO) in the entire temperature range: i.e. T_m (melting temperature) to T_g (glass transition temperature).

Keywords: Gibbs free energy difference (ΔG), polymeric melts

PACS: 60, 65, 65.60.+a

* *apratapmsu@yahoo.com*

INTRODUCTION

The Gibbs free energy difference (ΔG) between the under cooled liquid and the corresponding equilibrium solid phases is found to be an important parameter in predicting the glass forming ability. Several investigators [1-5] have suggested expressions for evaluation of ΔG. In present paper, we have suggested an expression which has been derived assuming hyperbolic dependence of ΔC_p with temperature. The aim of the present investigation is to study the thermodynamic behavior of the glass forming polymeric melts.

THEORETICAL EXPRESSION

The difference in Gibbs free energy between the liquid and crystalline phase is given by

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

where

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \qquad (2)$$

and

$$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \qquad (3)$$

where, T_m is the melting temperature, ΔS_m is the entropy of fusion and ΔH_m is the enthalpy of fusion.
Putting Eq. (2) and Eq. (3) in Eq. (1) and solving it, we get,

$$\Delta G(T) = \left[\Delta H_m - \int_T^{T_m} \Delta C_p dT\right] - T\left[\Delta S_f - \int_T^{T_m} \Delta C_p \frac{dT}{T}\right] \qquad (4)$$

$\Delta C_p{}^m = C_p^l - C_p^x$, is the difference in specific heats of the liquid and corresponding crystalline phase.

One expression for Δ*G* is given by Mishra and Dubey [6] based on hole theory of liquids leads to the following expression for ΔG:

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{2T}\left(1 - \frac{2}{3}\frac{T_k}{T_m}\frac{\Delta T}{T}\right) \qquad (5)$$

Where T_k = Kauzmann temperature, $\Delta T = T_m - T$
Another expression proposed by Lad et al [7] for bulk glass forming alloy is;

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left[\frac{4T^2}{(T+T_m)^2}\right] \qquad (6)$$

In Eq .(6), ΔC_p is taken as constant but, ΔC_p does not remain constant in the entire undercooled region, for all glass forming systems.
For such systems, in which the specific heat increases considerably with undercooling, ΔC_p can be expressed as

$$\Delta C_p(T) = \frac{\Delta C_p{}^m T_m}{T} \qquad (7)$$

$\Delta C_p{}^m$ is the difference in the specific heats at the melting point. Substituting this value of ΔC_p in Eq. (4), we can get

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \Delta C_p{}^m T_m \left[\ln\frac{T_m}{T} - \frac{\Delta T}{T_m}\right] \qquad (8)$$

This expression of Δ*G* has been utilized for evaluating the GFA of bulk metallic glasses by Heena et al [8]. Here we have calculated Δ*G* for glass forming polymeric melts using Eq. (8).

RESULTS & DISCUSSION

The result of ΔG for PA6(fig.1) shows that our result (Eq.8) and the result of Mishra *et al.* (Eq.5) fall very close to experimental data. From the result for PPO (fig.2) we can see that our result (Eq.8) and the result of Mishra *et al.* (Eq.5) slightly underestimate in the

Proceeding of International Conference on Recent Trends in Applied Physics and Material Science
AIP Conf. Proc. 1536, 655-656 (2013); doi: 10.1063/1.4810397

entire undercooled region. On the other hand, the results of Lad *et al.* (Eq.6) show large variation in the lower temperature range i.e. at large undercooling. The result of Lad *et al.* (Eq.6) underestimates the experimental data because the temperature variation for ΔC_p has not been accounted and approximation in Taylor series has been taken.

The parameters used for the calculations of ΔG for these systems are given in Table.1.

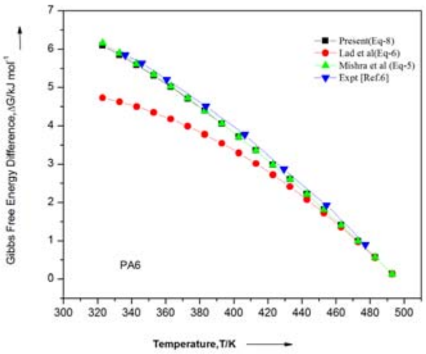

FIGURE 1. Gibbs free energy difference, ΔG as a function of temperature, T for polyamid-6 (PA-6)

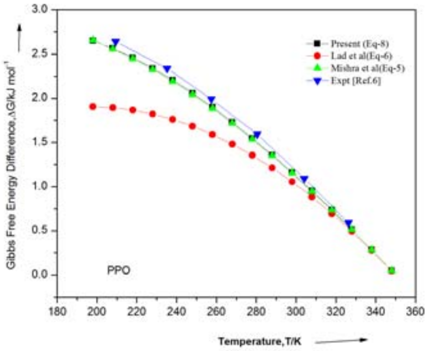

FIGURE 2 Gibbs free energy difference, ΔG as a function of temperature, T for polypropylene oxide (PPO)

CONCLUSION

The expression for the thermodynamic parameter ΔG based on the hyperbolic variation of ΔC_p describes the correct temperature dependence for glass forming polymeric melts. These polymeric samples have fairly good glass forming tendency owing to smaller value of ΔG.

TABLE 1 Parameters used for calculations [6]

System	Ti=Tg (K)	Tk (K)	Tm (K)	Tk/Tm (K)	ΔHm (kJ/mol)	ΔCp^m (kJ/mol-K)	ΔS_m (kJ/mol-K)
PA6	323	252.5	496	0.51	21.814	0.03815	0.04396
PPO	198	156.7	350	0.45	8.4	0.02198	0.024

REFERENCES

1. C.V.Thompson, F. Spacepen , ActaMetall, 1979,27,pp.1855-9.
2. J.D.Hoffman , J. Chem. Phys., 1958,29,pp.1192-3.
3. D.J.Turnbull , Appl. Phys. 1950,21,pp.1022-8.
4. D.R.H.Jones ,G.A. Chadwick , Phil Mag 1971,24,pp.995-8.
5. L.Battezzati,E.Garrone,Z.Metallika,1984,75,pp.305
6. R.K.Mishra , K.S.Dubey, J of Thermal Analysis and Calorimetry,2000, 62,pp.687-702.
7. K.N.Lad , K.G.Raval , Arun Pratap, J Non-Crystalline Solids,2004,334&335,pp.259-62
8. H Dhurandhar , T.L.Shanker Rao ,K.N. Lad, A Pratap, Philosophical Magazine letters,2008,pp.239-49