Macromol. Symp. ***148***, *15–30 (1999)*

ENTHALPY RECOVERY IN POLYMERIC GLASSES : DOES A CORRELATION EXIST BETWEEN THE EMPIRICAL (T-N-M) RELATIONSHIP PARAMETERS AND THE GLASS STRUCTURES ?

J.M.Saiter*, G.Denis and J.Grenet

Laboratoire d'Etude et de Caractérisation des Amorphes et des Polymères, EA 1292,
Faculté des Sciences, Université de Rouen, 76830 Mont Saint Aignan CEDEX, France
Contact Author : Jean Marc Saiter Tel : 00 2 35 14 66 32, Fax : 00 2 35 14 68 82,
email : Jean-Marc.Saiter@univ-rouen.fr

Abstract

To characterize the enthalpy recovery which appears during physical aging in glassy materials and especially in glassy polymers, the empirical Tool-Narayanaswamy-Moynihan (TNM) relationship for the relaxation time is widely used. This relationship depends essentially on three parameters, the apparent activation energy Δh*, the non linearity parameter x and the fictive temperature T_f. Even if a great amount of data (x, Δh*) can be found in the literature, no direct correlation between the values of these parameters and the engaged structures are available. On the one hand, using some polymers like Poly(ethylene terephthalate), Polymethyl(α-n-alkyl)acrylates and three dimensional epoxy networks for which structural changes are controlled and on the other hand, using some recently published results concerning other materials including inorganic polymers (Ge-Se and Ge-Te glasses), we show that it is possible to propose some interesting tendencies. In particular it is shown that the value of x depends on the intermolecular strength for organic polymers and on the connectivity for inorganic polymer.

CCC 1022-1360/99/$ 17.50+.50/0

Introduction

The aging of glasses and consequently of polymers can be understood by reference to the typical schematic enthalpy temperature diagram, presented in figure 1a. On cooling from an equilibrium liquid, the viscosity of the medium could suddenly increase at T_f [1]. This temperature, called fictive temperature, depends on the cooling rate and could be referred as the glass transition one T_g in a first approach. For a temperature $T_a < T_f$ the glassy state is reached. It is characterized by an excess of enthalpy and consequently the enthalpy will reduce towards equilibrium ($H_{eq\ (Ta)}$ on figure 1A), if an aging is performed at T_a [2]. During an aging, the energy loss (δh) can be easily determined from calorimetric investigations. Indeed, as shown on figure 1b, heating a no aged glass leads to the characteristic calorimetric curve on which the glass transition occurs as a ΔC_P step, while an endothermic peak at the glass transition is observed for the aged glass. Depending on the aging duration, the temperature and the magnitude of this peak will increase and the endothermic peak area is directly proportional to δh.

To obtain a theoretical description of the variations of δh with the aging duration, many approaches were proposed. Most of them are summarized in references [3] and [4]. Practically in all these approaches, the isothermal relaxation of enthalpy H is described by a kinetic equation of the form [5] :

$$\frac{\partial H}{\partial t} = -\frac{H - H_e}{\tau} \qquad (1)$$

where H_e is the equilibrium enthalpy at the temperature T_a, t is the aging time and τ the relaxation time.

It is now well established that τ depends on both the temperature T and the structure (characterized by T_f) and the most widely employed analytical expression used to define this dependence can be attributed to Tool [6, 7], Narayanaswamy [8] and

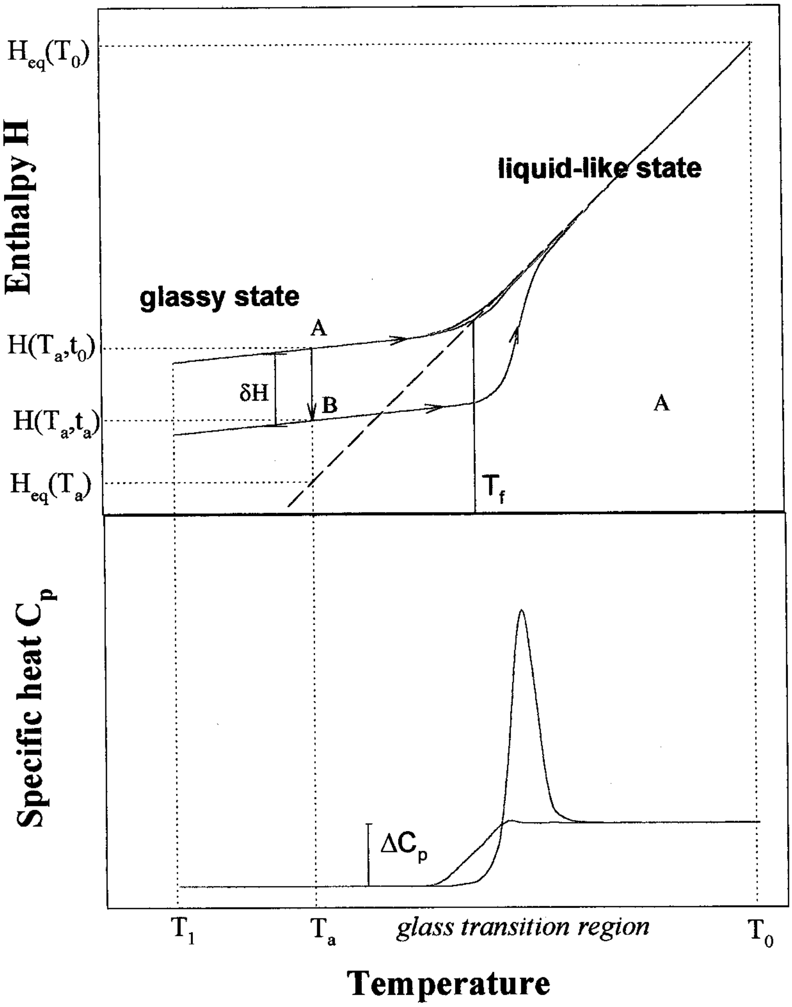


Figure 1 : Enthalpic variations observed on a glass during aging, performed at an annealing temperature T_a lower than T_g and associated calorimetric curves. This diagram allows the definition of the fictive temperature T_f.

Moynihan [9], which leads to the Tool-Narayanaswamy-Moynihan also called the TNM relationship :

$$\tau = \tau_0 \exp\left(\frac{x\Delta h^*}{RT}\right)\exp\left(\frac{(1-x)\Delta h^*}{RT_f}\right) \qquad (2)$$

where τ_0 is a constant, x is the Narayanaswamy parameter also called the non linearity parameter, $1 \geq x \geq 0$, and Δh^* is the apparent activation energy.

The TNM parameters are theoretically characteristic of the material. Nevertheless, it has been reported that correlation between polymer structures and TNM parameter values are not still clear. In this respect, Hodge [4] has summarized a substantial amount of data collected on materials exhibiting ionic or covalent bonds and on more simple molecular glasses. He concludes that the values of Δh^* are often too large to be considered as simple transition state activation energies and that a physical interpretation for x does not really exist.

In fact, we believe that the comparison of data collected in the literature requires many precautions. Firstly, it is known that the value of the TNM parameters depends on the molecular weigh of the polymer [10], on its tacticity [11-12]. Secondly, it is also known that the method used to extract the data from the experimental curves can lead, for the same material, to different values of the TNM parameters. For instance, for a-PMMA, x values as different as 0.19, 0.13 and 0.37 were proposed respectively in references [13], [12] and [14]. To compare results of different origins to find a correlation between TNM parameters values and polymer structures, it is of prime importance to use the same experimental methods and to work on materials for which the structure or the structural modifications are well known. This is our goal.

In the following, the peak shift method [15] will be used to obtain the values for x. Results concerning linear polyester, three dimensional networks for the traditional polymers and inorganic covalent glasses as Se based alloys will be discussed.

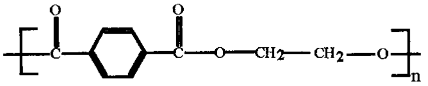
Material and method

The linear polyester polymers used in this work are a poly(ethylene terephthalate) film or PET supplied by Carolex S.A., a poly(ethylene naphthalene 2,6-dicarboxylate) film or PEN supplied by Amoco Chemical Company, a copolyester of PET and PEN or PETN8 (92% of DMT and 8% of NDC), a poly(cyclohexane 1,4-dimethyl terephthalate) film or PCT supplied by Eastman Chemical. The chemical formula of these polyesters are presented in figure 2. All the polymers were fully amorphous. The values of molecular weights are for these polymers in the range 25000 to 31000 $gmol^{-1}$.

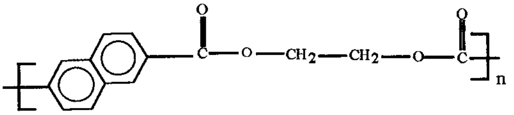
Polymethyl(α-n-propyl)acrylate (C3), Polymethyl(α-n-pentyl)acrylate (C5), Polymethyl(α-n-octyl)acrylate (C8) were synthesized as described previously [16]. Molecular weights Mn are respectively, 39000, 55000 and 24400, for C3, C5 and C8 with a polydispersity lying between 1.5 and 2, determined by size exclusion chromatography in toluene at room temperature with polystyrene standards for calibration. The Mn values correspond to those obtained on the plateau of $Tg = F(Mn)$ [16], which limit the effects of Mn on the variability of x and Δh^* values. The chemical formula are also presented in figure 2.

Two different epoxy resins were used for three dimensional networks,. The first one (called Epoxy 3) is a DGEBA (DER 332, Dow Chemical) cured with a poly(propylene oxyde) (Jeffamine D230 supplied by Texaco Chemical Company) or PPO230, and the second one (called epoxy 4) is the same DGEBA cured with a Jeffamine D400 or PPO400. Stochiometric content of resin and hardener were mixed and heated at 70°C, under vacuum, for half an hour, then molded and cured for 24 hours at 100°C and finally post cured for 2 hours at 120°C. The chemical formula are reported on figure 2.

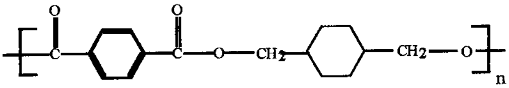
Figure 2 a



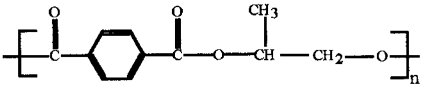
PET



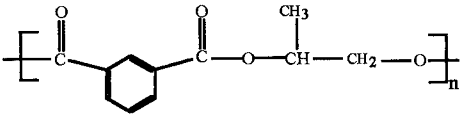
PEN



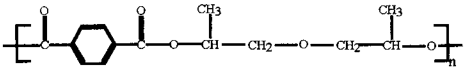
PCT



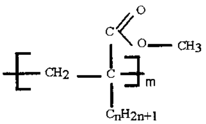
PPTP



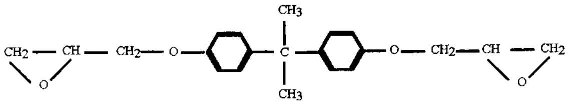
PPIP



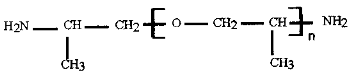
PDPT



Poly(methyl(α-n-alkyl)acrylate



DGEBA DER 332



n = 2.7 for D230, n = 5.6 for D400

Figure 2b

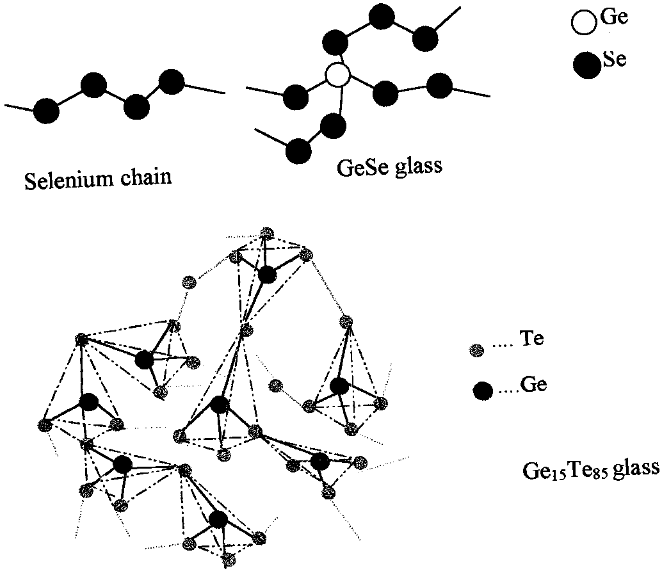


Figure 2 : The different materials and associated structures which have been used in this work

For inorganic glasses, we have used, Se, Ge_xSe_{1-x} and $Ge_{15}Te_{85}$ vitreous chalcogenide materials. Each sample of the expected composition was obtained from a mixture of both elements (99.999 % purity) in a granular form. The mixture was introduced into a quartz ampoule and sealed in a vacuum of 10^{-3} Torr. Then, the ampoules were placed in a horizontally rotating oven and annealed at 1273 K during more than 10 h. Finally they were water quenched.. The vitreous nature of the sample was checked at room temperature by X-ray diffraction.

Method

The values of x have been determined by the peak-shift method [15], which examines the response, on heating, of glasses that have been formed by cooling below T_g at a rate q^-, and then annealed at T_a in order to allow the enthalpy of the glass to reduce by an amount δh. During heating at a rate q^+ in the DSC experiment, the endothermic response passes through a maximum at a temperature T_p, which depends upon δh. This enthalpy loss, δh, is found experimentally from the area difference between the scan on the annealed glass and a scan on an unannealed glass (reference scan) made for the same cooling and heating rates. The dependence of T_p on δh can be used to define a dimensionless shift :

$$\hat{s}(\overline{D}) = \Delta Cp\left(\frac{\partial Tp}{\partial \delta h}\right)_{q^-,q^+,Ta} \tag{3}$$

where the normalizing factor ΔC_p is the difference between the specific heat capacities of the liquid C_{pl} and of the glass C_{pg}, evaluated for an unannealed glass at the midpoint of the glass transition region. The shift can be shown to be related to, and depend sensitively upon, x according to a master curve, which has been derived theoretically.

Thus, by representing the value of $\hat{s}(\overline{D})$ on the master curve, it is possible to obtain the value of x. This approach is known as the peak-shift method.

Results and discussion

For all our vitreous materials, the values of the x parameter obtained through the use of the peak shift method are reported in table 1. Whatever the material, for our linear polyester polymers practically the same x value is obtained. Only PCT for which a cyclohexylene ring is inserted in the main chain presents some small sensible variations, with a lower x value. At this stage of the data analysis, all these differences are not enough significant to allow a correlation between the x values and the structures engaged in these materials. These results may be compared with those obtained by P.Cortes et al [17-18], on an other family of polyesters. In this last work the values of the TNM parameters (values reported in table 1) for a poly(ethylene terephthalate) PET, a poly(propylene terephthalate) PPT, a poly(propylene isophtalate) PPI and a poly(dipropylene terephthalate) PDPT, are determined with exactly the same method as used in this work. The chemical formula of these polyesters are also reported in figure 2. For PET, the results obtained are the same than ours. On the other hand, with this series of polyesters, this is the effect of the introduction of a methyl group pendant from the main chain on the x value which can be investigated if we compare the results obtained for PET and PPT, while this is the effect of the ring substitution on the x value which can be expected by comparison of results obtained on PPT and PPI. It is clear that the ring substition leads to small changes in the values of x. The same conclusions appear if we compare these results to those obtained on PEN, on PCT, and on PETN8 copolymer. For these polymers, we may suppose that molecular movements takes place mainly along the flexible parts of the chain and that rings do not move. Rings only act as "branching molecules" or hard block segment. In other words, the modification of the

material	**PET**	**PEN**	**PETN8**	**PCT**
x	0.49	0.50	0.48	0.45
Mn (g/mol)	31000	25000		25000
material	**PET [17]**	**PPTP [17]**	**PPIP [17]**	**PDPT [17]**
x	0.46	0.57	0.61	0.26
Mn (g/mol)	20000	9300	11000	9700
material	**C1 [14]**	**C3 [14]**	**C5 [14]**	**C8 [14]**
x	0.37	0.45	0.49	0.55
Mn (g/mol)		39000	55000	24400
material	**Epoxy 1 [19]**	**Epoxy 2 [20]**	**Epoxy 3**	**Epoxy 4**
x	0.41	0.41	0.36	0.47
Rate of cure	70	100	100	100
material	**Se [25]**	**Se_8Ge_{92} [25]**	**$Se_{12}Ge_{88}$ [25]**	**$Te_{15}Ge_{85}$**
x	0.57	0.60	0.50	0.67

Table 1 : values of the TNM parameters for linear polyesters, three dimensional networks and chalcogenide glasses.

size or of the nature of these "branching molecules" do not change the x value. Because of the existence of the cyclohexylene ring occurring in the PCT formula, significant structural changes in term of main chain flexibility could be expected. Nevertheless the x value obtained with this material is very close to those obtained for the other polyesters as PET and PEN. This is for PDPT that the smallest x value is obtained, and the magnitude of the difference observed between this value and all the other ones is enough important to be significant. This is the linear polymer for which the flexible chain is the longest. Thus, from these first results, we may conclude that subsequent variations on the x values are observed mainly if important modifications occur in the soft segment of the main chain, while modifications of the hard block part of the chain do not lead practically to observable x variations. In the series of linear polymers, this is for poly(α-n-alkyl)acrylates that the most spectacular x variations are observed. Indeed, greater the alkyl chain, greater the x value. Using, the schematic diagram displayed on figure 3, it is very tempting to connect the x variations to the distance which separates two main polymeric chains. Thus, it appears that the values of x are more sensitive to modifications of the intermolecular forces, rather than modifications of the intra molecular forces.

For epoxy resins, we have in table 1 added the results obtained by S.Montserrat et al [19] and J.M.Hutchinson et al. [20]. This epoxy system is derived from diglycidyl ether of bisphenol-A cured by methyl-tetrahydrophthalic anhydride with accelerator A result concerns a partially cured resin which has reached a rate of transformation of 70% (called Epoxy 1 in table 1) while a second one is obtained on the same system with a rate of transformation of 100% (called epoxy 2 in table 1). One more time, the same method is used to extract the x value from the calorimetric data. With these rates of transformation, we may suppose, in a first approximation, that this is the number of connected segments which is changed rather than the average distance which separates the main chains (as displayed on the schematic diagram on figure 3). It was found

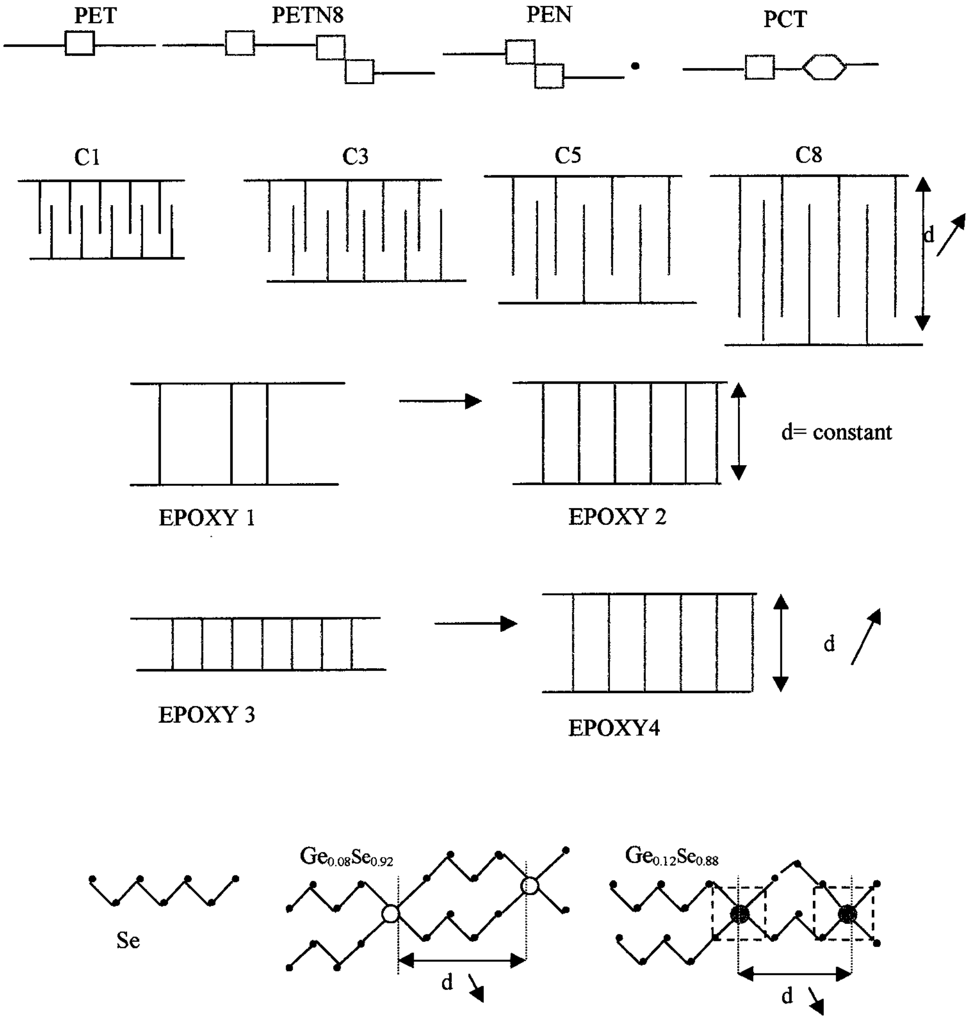


Figure 3 : Schematic diagrams showing the structural modifications which occur in the different materials studied in this work.

exactly the same x value for both cases. We may now compare these results with those obtained on our two epoxy resins for which this is the length of the hardener which increases by using a PPO 230 or a PPO 400. In this case, the value of x increases as the length of the hardener increases (also displayed on the schematic figure 3). One more time, it appears clearly from these results that this is mainly the magnitude of the intermolecular forces which is involved in the x value.

For the Ge-Se system, each atom is known to respect the 8-N rule. Thus the coordination number of Ge is four and the coordination number of Se is two. The structure of these glasses are reported in figure 2. In previous works [21-25] the structural relaxation of Ge_xSe_{1-x} glasses was investigated and the results obtained on this system (reported in table 1), have been explained through the movement abilities of "Se cell" (made of three adjacent Se atoms) and of "Ge cell" (including an atom of Ge and the four connected Se atoms) into a medium in which the dimensionality varies with the composition. This dimensionality increases from 1 for linear pure Se glass to 2 with the development of a cross-linked structure when Ge is introduced in the Se glassy medium. To resume, increasing the Ge content leads simultaneously to a decrease of the number of relaxing units and to a decrease of the length of the relaxing chains which are included between two successive Ge cells. Finally, the number of "Se cell" vanishes for compositions beyond 12 at.% of Ge and for x > 12 at.% the relaxation phenomena disappear (in a time scale experimentally accessible). Thus, in this system, relaxation takes place by movements of Se atoms which are in the "Se cell", while the $GeSe_4$ tetrahedral units remains blocked. The value of x obtained for this system decreases as the Ge content increases. In this case, both the intra and intermolecular forces are modified when the Ge content increases. Thus, a decrease in the x value is one more time connected to the increase of these forces.

On the other hand, for $Ge_{15}Te_{85}$, the value of x = 0.67 found in this work is relatively high. For this glass, the coordination number of Ge atoms was determined from EXAFS measurements and it was found that each Ge atom is connected to 4 Te atoms [26-27]. Thus, as for GeSe system, the Ge tetrahedral structure exists in this $Ge_{15}Te_{85}$ glass and at this Ge content, it was shown that each tetrahedra are connected together by at least one Te atom, as shown on figure 2 [28]. The x value obtained for the $Ge_{15}Te_{85}$ glass is greater than the value obtained for pure Se. The,$Ge_{15}Te_{85}$ glass exhibits a behavior expected for a linear structure rather than expected for a two or three dimensional network. Thus, for $Ge_{15}Te_{85}$, the molecular relaxations take place by movements which imply the $GeTe_4$ tetrahedral units. In this situation, the intermolecular forces must be low. This point is confirmed by the very low value for the relaxation time ($\tau_{Tg\text{-}10°C} \approx 100h$), requires to obtain, at Tg-10°C, a fully relaxed $Ge_{15}Te_{85}$ glass.

From all these results, it appears that x values must be connected mainly with the magnitude of intermolecular forces. Finally, if we come back to formula 2, which defines the relaxation time τ, a great value for x decreases the effect of the second exponential which characterizes the effects of the structure on τ. Thus, lower the intermolecular forces, greater the ability for the molecular units, which are involved in the relaxation process, to move independently one of the other, consequently lower are the cooperative effects and lower must be the x values. This is experimentally observed in this work.

Conclusion

In this work, we have presented new results concerning the values of the non linearity parameter x which occurs in the Tool-Narayanaswamy-Moynihan relationship defining the relaxation time for the enthalpy recovery. With the help of other results, we have shown that, if the comparison of data are performed on materials for which the structural modifications are well known and if the method used to extract the x value from calorimetric experiments is not changed, it is possible to correlate x values and material structures. All the results show that this is mainly the intermolecular forces which exist between the main chains which govern this correlation ; greater the intermolecular forces, lower the x values

References

1 C.A.Angell, J. of Non-Cryst.Solids, 131-133, (1991), 13

2 L.C.E. Struik, *Physical ageing in amorphous polymers and other materials,* Elsevier, Amsterdam, 1978

3 J.M Hutchinson, Prog. Polym. Sci., 20, (1995), 703,

4 I.M. Hodge, J. of Non-Cryst.Solids., 169, (1994), 211

5 C.T. Moynihan, A. J.Easteal, M.A. deBolt and J. Tucker, J. Am. Ceram. Soc., 59, (1976), 12

6 A.Q., Tool, J.Am. Ceram. Soc., 29, (1946), 240

7 A.Q. Tool, and C. Eichlin, J.Am. Ceram. Soc , 14, (1931), 276

8 O.S. Narayanaswamy, J.Am. Ceram. Soc., 54, (1971), 491

9 C.T. Moynihan, A. J. Easteal, J.Wilder and J. Tucker; J. Phys. Chem., 78, (1974), 2673

10 V. P.,Privalko, S. S. Demchenko, Y. S. Lipatov, Macromolecules, 19, (1986), 901

11 J.T.Tribone, J.M. O'Reilly, and J. Greener, Macromolecules, 19, (1986), 1732

12 I. M. Hodge, J. of Non-Cryst.Solids, 131-133, (1991), 435

13 I. M. Hodge, Macromolecules, 20, (1987), 2897

14 M.E.Godard, J.M.Saiter, P.Cortes, S.Montserrat, J.Hutchinson, F.Burel, and C.Bunel, J. Polym. Sci., B, Polym. Phys. Ed., 36, (1998), 583

15 J.M. Hutchinson, and M. Ruddy, J. Polym. Sci., B, Polym. Phys. Ed., 28, (1990), 2127

16 F.Burel, J.P.Couvercelle, C.Bunel, and J.M.Saiter, J. Macromol. Sci., Pure Appl. Chem. A(32), 6, (1995), 1091

17 P.Cortes, and S.Monserrat, J. Polym. Sci., B, polym. Phys. Ed, 36, (1198), 113

18 P.Cortes, and S.Monserrat, J. of Non-Cryst.Solids, 172-174, (1994), 622

19 S. Monserrat, P. Cortes, A. J. Papin, K. H. Quah, and J.M. Hutchinson, J. of Non-Cryst.Solids, 172-174, (1994), 1017

20 J.M. Hutchinson, D. McCarthy, S. Monserrat, and P. Cortes, J. Polym. Sci., B, polym. Phys., Ed., 34, (1996), 229

21 J.M. Saiter, A. Assou, J. Grenet, and C. Vautier, Phil. Mag. B, 64, (1991), 33

22 J.M. Saiter, J Grenet, and P. Lebaudy, J. of Non-Cryst. Solids, 131-133, (1991), 524

23 J.M. Saiter, A. Hamou, and C. Vautier, J. of Non-Cryst. Solids, 172-174, (1994), 580

24 J. Grenet, J.P. Larmagnac, P. Michon, and C. Vautier, 1981, Thin Solid Films, 76, 53

25 P. Cortes, S. Montserrat, J. Ledru, and J.M. Saiter, J. of Non-Cryst. Solids 235-237, (1998), 552

26 J.M. Saiter, Q. Ma, S. Benazeth, M. Belhadji, and C. Vautier, Mat. Letters, **19,** (1994), 287

27 J.M. Saiter, S. Benazeth, Q. Ma, M. Belhadji, and C. Vautier, 1995, J. of Non-Cryst. Solids, 192-193, 369

28 Y.Kameda, O.Uemura, T.Usiki, Mat. Trans. , JIM, 37, (1996), 1655