A. Danch

**The August Chełkowski Institute of Physics,
Silesian University,**
40-007 Katowice, ul. Uniwersytecka 4, Poland,
danch@us.edu.pl

On the influence of the supermolecular structure on structural relaxation in the glass transition zone: free volume approach

1. Introduction

Segmental relaxation, which occurs near the glass transition temperature, entails the micro-Brownian motion of several units (mers) of a macromolecule. Thus, the shape of viscoelastic or dielectric dispersion is expected to reflect in some manner the supermolecular structure of polymers. It is difficult both to recognise and unambiguously identify the relaxations which arise from similar mechanisms in different polymers. However, both numerous suggestions on the origin of the α relaxation and the experimental data which have been reviewed and collected [1-3] show a common feature of this relaxation for polymers. While increasingly detailed considerations of the structural relaxation to physical properties have very likely advanced the understanding of the molecular mechanisms of this process, another useful approach is to look for the empirical relationship which applies to α relaxation in more than one polymer. The glass transition temperature (T_g) itself has been related to chemical structure [1,4]. Additionally, for polymers, various correlations between the temperature and time dependencies of segmental relaxation (α relaxation) have been demonstrated [3-4]. However, attempts to relate the temperature dependence of the relaxation time (τ) to the thermodynamic parameters measured in different experiments, e.g. differential scanning calorimetry (DSC) and positron annihilation (free volume), are scarce. These relations involve activation parameters and other thermodynamic quantities (the isobaric coefficient of thermal volume expansion, isothermal compressibility, and crystalline melting temperature). The relatively large values of the activation parameters for this relaxation which have been observed in mechanical or dielectric experiments (DMTA, DETA) suggest that large molecular segments are involved. Widespread experience demonstrates that the properties of materials do not depend on the chemical constitution alone, but also on the mutual arrangement and the dynamics of the molecules

Abstract

The idea of two miscellaneous amorphous fractions in polymer is discussed. The effect of free volume on the segmental relaxation behaviour is examined for a wide range of polymers. The orientation of the amorphous regions induced by semi- or liquid-crystallinity results in the appearance of constrained and unconstrained amorphous structures. In this paper, which better describes α relaxation, both types of amorphous fractions are distinguished. One fraction behaves as a bulky amorphous material ('real'), whereas the other one ('semi-ordered') behaves as a partially ordered structure. This results in two types of loss peaks interspersed along the temperature scale. The heights of both loss peaks are quite sensitive to the amount of free volume. α relaxation is deeply related to glass transition, although these two phenomena are distinct. Differential scanning calorimetry, dynamic mechanical thermal analysis and positron annihilation were used to study the effect of specimen treatment on the assignment of the glass transition event associated with 'semi-ordered' amorphous phases. In a series of experimental studies of chain mobility and free volume, our attention has been given to elucidating the correlation between glass transition, α relaxation and the free volume of polymeric system.

Key words: *polymers, free volume, α relaxation.*

(supermolecular structure). To evaluate the relationship mentioned above, activation parameters are needed. In a number of instances, DMTA or DETA, the measurements have not been made over a frequency range which is great enough to permit a sufficiently accurate determination of these parameters. Moreover, two overlapped α relaxations can be recognised in many cases [5-8].

In this paper, a new relationship between the relaxation time of the α relaxation and the supermolecular structure parameters is presented. Specifically, it will be shown that there is a constraint on this segmental relaxation from interaction with neighbouring, nonbonded segments (mers) in polymers. This correlation of intermolecular cooperativity and the free volume will be demonstrated. It is tempting to think that the mechanism of the structural relaxation is important for both the glass transition and melting. Using this approach, the present study provides an interpretation of how supermolecular structure governs the magnitude of activation parameters. In this paper, a summary and analysis of the experimental data pertinent to the free volume approach are presented.

2. Amorphous phase – experimental evidence

It is commonly accepted that α relaxation reflects the segmental motion of the chains built (located) in an amorphous phase of polymer. However, the arrangement of these chains strictly depends on the conditions of the sample's preparation. Altering the thermal history of a sample changes the physical properties of the polymer. It has been previously noted that thermal treatment might drastically influence the supermolecular structure [9]. Many polymers, especially those with simple chemical structures and hence weak intermolecular coupling, are semicrystalline. In such a case, and for the liquid-crystal polymers which the crystal-amorphous interphase exists in, a new factor affecting the supermolecular structure of the amorphous regions was postulated [10-12]. The domain of long-range order, which exists in semi- and liquid-crystalline systems, distinctly influences the arrangement of the chains which build the amorphous regions. This results in the appearance of two amorphous fractions in one polymeric system, constrained and unconstrained. The former behaves as if it were a bulky amorphous material, whereas the later behaves as if it were a partially ordered structure. The bulk amorphous structure, unperturbed by the presence of the crystals, exhibits typical stepwise transition at T_g (DSC) and a single discrete peak (DMTA, DETA). T_g-distribution and two relaxation peaks are found when the system included the crystals located

in the amorphous matrix [5-8]. It must be emphasised that the co-existence of the amorphous and crystalline phases results in different properties of the amorphous phase. It was thus postulated that the co-existent amorphous phase could be treated as a 'fingerprint' of the ordered phase, crystalline or liquid-crystalline [8].

No rule can be stated which would properly describe the α relaxations observed in the different polymeric systems. When the line of Arrhenius' plot exhibits some curvature, it means that the molecular motion depends on a free volume. As was established, the real amorphous fraction is reflected as a stepwise transition in DSC curves, and the Vogel-Fulcher relation is used for the description of the α relaxation exhibited by this supermolecular structure. The semi-ordered fraction is recorded in DSC curves as a small step of a C_p value and an endothermal peak following the step, and the Arrhenius relation is used for the description of the α relaxation [2-3,5-8]. Experimental evidence shows that at least two fractions of the amorphous phase should be exhibited by the polymeric systems. Therefore we postulate the division of the amorphous supermolecular structures and the α relaxations related to them into three groups: an (A_g) structure which never creates crystalline forms; an (A_c) structure which may include crystalline forms and the supermolecular structure which is completely perturbed by them (polymers with high degree of crystallisation); and an (A_p) structure of semi-crystalline polymers, where perturbation is not strong (a medial case between A_g and A_c).

3. Description of the α relaxations

3.1. Assumptions

The mechanism of segmental relaxation involves main-chain motion over large length scales. This intramolecular cooperativity requires intermolecular interaction, which might be represented in the description by the parameter of free volume. In order to find one mathematical formula describing the α relaxations, the following assumptions are made:
a) there is a thermally activated process (Arrhenius' type of relation, $\tau \rightarrow f(1/T)$);
b) the number of mers taking part in the molecular motion increases with temperature due to the increase in free volume ($n_\alpha \rightarrow f(T)$);
c) the activation enthalpy of the motion decreases with temperature ($\Delta H_\alpha \rightarrow f(1/T)$);
d) the activation enthalpy, $\Delta H\alpha$, is a function of the number of mers and of the enthalpy of the macromolecules' interaction (($\Delta H_\alpha \rightarrow f(n_\alpha, H_i)$);
e) the relaxation time is strictly related to the free volume of the polymeric system;
f) the H_i value decreases with temperature due to the increase in free volume.

The temperature-dependent relaxation time should be given by a formula where the fitting parameters must possess physical interpretation; furthermore, it should be possible to obtain them from other measurements (DSC, a free volume parameter).

3.2. Formula- general description

The empirical relation referred to the above assumption combines the Arrhenius and the Vogel-Fulcher relations. According to the model of relaxation, the formula is given by

$$\tau = \tau_l \cdot \exp(\frac{\Delta H_\alpha}{\Delta C_p(T_g)} \cdot \frac{1}{T}) \qquad (1)$$

where:
τ_l- the relaxation time at high temperature ($T \rightarrow \infty$, a mathematical approximation; in practice, it is the τ value in a liquid state at a temperature below that of polymer decomposition).
ΔH_α- the enthalpy of activation of the α relaxation.
$\Delta C_p(T_g)$- the change of the specific heat taken at the glass transition temperature (all values, taken from DSC measurements, are always obtained for the zero heating rate extrapolation).

The rather high values of the activation enthalpy obtained from the Arrhenius relation for experimental data [2-4] suggest that this parameter most likely varied with temperature. As was postulated above, this parameter should be a function of the number of the mers taking part in the relaxation (n_α) and the enthalpy of intermolecular interaction (H_i).

$$\Delta H_\alpha = n_\alpha \cdot H_i \qquad (2)$$

Both n_α and H_i are the functions of the temperature given by the following formulae:

$$n_\alpha = n_l \cdot \left(1 - \frac{1}{1 + \left(\frac{T}{T_c} \right)^\beta} \right) \qquad (3)$$
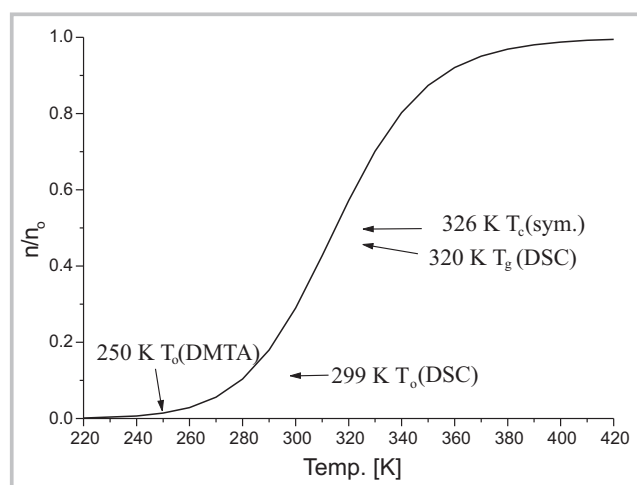

Figure 1. Temperature dependence of the number of mers taking part in the α relaxation. T_c- parameter of the fitting procedure, T_g and T_o taken from DSC and DMTA measurements, respectively.
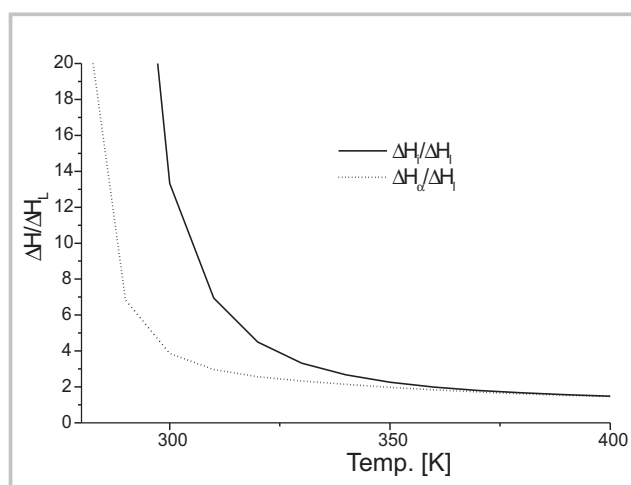

Figure 2. An example of temperature dependencies of the enthalpy of activation of the relaxation (dotted line) and the enthalpy of intermolecular interaction (solid line).

$$H_i = H_l \cdot \exp\left(\left(\frac{\Delta T^*}{T - T_0}\right)^2\right) \qquad (4)$$

where: $\Delta T^* = T_m - T_t$, T_m - the melting temperature of the crystalline (liquid-crystalline) phase, T_t - the temperature of the transition involving the α relaxation, T_0 - the temperature at which the relaxation starts.

The β parameter is calculated using the experimental thermodynamic parameters taken from DSC measurements after their zero heating rate extrapolation. The following definition of the β parameter is postulated:

$$\beta = 2 \cdot \left(\frac{T_g}{T_m - T_t}\right)^2 \qquad (5)$$

In order to adopt equation 1 for all the cases described in literature, some further assumptions must be made. This allows the two types of relaxation time relation mentioned above to be obtained, these being realised by the modified functions similar either to the Arrhenius or the Vogel-Fulcher functions. The assumptions arisen from the experimental evidences are as follows for the different fraction of the amorphous phase:

- the 'real' amorphous phase (A_g), $T_m = 0$, $T_t = T_g$ which implies $\beta = 2$ and the adequate functions of the n_α and H_i variables
- the 'ordered' amorphous phase (A_c), $T_t = T_m$ which implies $\beta = \infty$, $n_\alpha = n_l$ and $H_i = H_l$
- the 'semi-ordered' amorphous phase (A_p), $T_g \leq T_t < T_m$ which implies $2 \leq \beta < \infty$ and the adequate n_α and H_i functions.

The available literature data does not provide the best possible test of equation 1. The possible errors of fitting are large because of the varied nature of both data and samples. A better test could be made if the experimental errors were reduced by making all measurements of mechanical and thermal
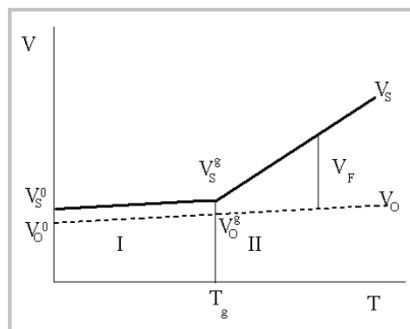

Figure 3. The relation between V_g, V_o and V_F in two temperature regions (below and above T_g).

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properties on the same polymer sample. Nevertheless, the data does tend to support the validity of equation 1, which is discussed in the next sections.

3.3. Free volume approach

The glass transition can also be defined from dilatometric data [4]. It may appear that the specific volume (V_S) as a function of temperature shows a tendency to form a straight line from which the T_g value is pointed out (Fig.(3)). The picture, presented below, schematically shows the temperature specific volume dependence and the relation between this volume and the occupied (V_o) and free (V_F) volumes. Generally speaking, their temperature dependencies might be represent by the linear type functions.

I temperature range: $T \leq T_g$

$$V_S = V_S^0 + \alpha_{S_1} \cdot T$$

$$V_O = V_O^0 + \alpha_O \cdot T$$

$$V_F = V_S - V_O = V_S^0 - V_O^0 = V_F^0 = V_F^g ,$$

with assumption: $\alpha_{S_1} = \alpha_O$

II temperature range: $T > T_g$

$$V_S = V_S^g + \alpha_{S_2} \cdot (T - T_g)$$

$$V_O = V_O^g + \alpha_O \cdot (T - T_g)$$

$$V_F = V_S - V_O = (\alpha_{S_2} - \alpha_O) \cdot (T - T_g) + V_F^0$$

$$\frac{V_F - V_F^0}{V_F^0} = \frac{\alpha_{S_2} - \alpha_{S_1}}{V_F^0} \cdot (T - T_g) \approx \frac{V_S^0}{V_F^0} \cdot \delta^* \cdot (T - T_g)$$

where:

$$\delta^* \approx \alpha_{S_2}^* - \alpha_{S_1}^* , \quad \alpha_{S_1}^* = \frac{\alpha_{S_1}}{V_S^0}, \alpha_{S_2}^* = \frac{\alpha_{S_2}}{V_S^g}$$

It is known from experiments that:

$$\alpha_{S_1} < \alpha_F < \alpha_{S_2} ,$$

therefore: $\alpha_{S_1}^* < \delta^* < \alpha_{S_2}^* \cdot \dfrac{V_S^g}{V_S^0}$, because

$$\alpha_F^* = \delta^* \cdot \frac{V_S^0}{V_F^0} .$$

The correlation between the parameters characterising free volume, the mechanical/dielectric and the calorimetric data is proposed.

$$\delta^* = \frac{A}{T_g \cdot \beta} , \qquad (6)$$

T_g - the temperature of the glass transition. The temperature is defined from the midpoint of the change in a heat flow vs. temperature curve (DSC).

β - the value can be obtained as a fitting parameter of the relaxation times data (DMTA, DETA). The same value should be obtained from the

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equation which defines this parameter (Eq.(5)).

A - the fitting constant.

δ^* - the value is taken from the free volume or specific volume measurements, $\delta^* \approx \alpha_{S_2}^* - \alpha_{S_1}^*$.

The description of the free-volume temperature variation presented above shows how to calculate the thermodynamic parameters describing the α relaxation, which is related to the adequate T_g value. The δ^* value may be obtained either directly from positron annihilation experiments or dilatometric measurements. Unfortunately, both experimental methods require the specific treatment of a studied sample as compared with DSC, DETA and DMTA. It is very well known that different regimes of sample preparation produce various supermolecular structures of polymers. Therefore, as will be demonstrated in section 4.2, the δ^* value obtained directly from experiments (δ^*(exp.)) and the δ^* value calculated from DSC/DMTA data (δ^*(cal.)) are different. This difference disappears when an adequate assumption is made concerning the type of the amorphous fraction which α relaxation occurs in.

4. Discussion of the δ^* value for the various amorphous fractions

4.1. Calculation from the definition equation 5

How accurate is the free volume relation equation 5? To address this question, the δ^* values were calculated and compared with the experimental results. In all the cases, as presented in Table 1, only the real amorphous fraction was taken into account. Such treatment implies that the case of the α_g relaxation occurred with $\beta = 2$ (calculated from the definition of the parameter, equation 5). δ^* is calculated with the assumption that A=1. The values extrapolated are required for calculation of the δ parameter. Because the temperatures were not indicated in an appropriate manner, the temperatures obtained for the 20 deg/min rate were taken from literature.

The diameter of the free volume sphere (R_F) was always calculated from the experimental data obtained at room temperature. The free volumes, found for the real amorphous fraction of PE, PP and PMP, are much higher then for the rest of the polymers. It is easy to see that

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Table 1. *Comparison of the parameters measured in different experiments: T_g, $\delta^*(cal)$ and R_F. The data which is taken from literature is indicated as an upper index: a-[13]; b-[14]; c-[15]; d-[8]; e-[16]; f-[17]; g-[18]*

Polymer	T_g [K]	$\delta^*(cal)\cdot 10^{-3}$ [K^{-1}]	R_F [nm]
cardo polyimid (PI)	662-669[a]	0.75-0.75	-
poly(ethylene) (PE)	153[b]	3.27	0.333[b]
poly(vinyl chloride) (PVC)	354-372[c]	1.41-1.34	0.270[e]
poly(vinyl alcohol) (PVA)	343-373[c]	1.46-1.34	0.227[e]
poly(propylene) (PP)	?	-	0.331[f]
poly(styrene) (PS)	353-378[c]	1.41-1.32	0.287[e]
poly(methyl pentene) (PMP)	293-319[d]	1.71-1.57	0.320[g]
poly(methyl methacrylate) (PMMA)	311[c] (iso) 378[c] (a)	1.61 1.34	0.277[e]

the choice of the measurement temperature was significant, as it was either above or below the T_g value of the studied polymer.

The series of the δ^* value of the chosen polymers with the decreasing order is: PE, (PP?) > PMP, PMMA > PVC, PVA, PS(?) > PI. One may conclude that the increase in the free volume with temperature for the small monomer is stronger as compared with the large monomer. However, the free volumes of the polymeric materials show an opposite tendency for the temperatures below T_g. This means that the smaller the molecule, the smaller the free volume exhibited.

4.2 Comparison with the experiments

4.2.1. Poly(ethylene)- semicrystalline polymer [9]

$\delta^*(cal)=3.27\cdot10^{-3}$ K^{-1}, the calculation was performed with the assumption that this amorphous fraction is the pure amorphous one that implies $\beta=2$. However, $\delta^*(exp.)$ calculated from the specific volume data is $1.10\cdot10^{-4}$ K^{-1} [19]. According to the model proposed in this paper also, the β parameter can be obtained from equation 1 as a fitting parameter of the experimental data. The $\beta(fit.)$ value is 59.08 ± 1.81 (DETA data [20]). However, the value of this parameter ($\beta(exp.)$), calculated from equation 6 for the dilatometric data ($\delta^*(exp.)$, $T_g=153K$) is 64.93. This value of the $\beta(exp.)$ parameter would suggest that the real amorphous phase does not exist in PE samples of a high degree of crystallisation. The Arrhenius type relation found for the relaxation time supports such a point of view. One may assume that the calculated $\beta(exp.)$ value is correct. In such a case, the calculated T_t value, as calculated from definition equation 5, is 368K. This would signify a strong influence of the crystals on the α relaxation.

4.2.2. Polynorbornene derivative- liquid crystalline polymer [21]

Two cases are taken into account:
- a smectic phase created with an unordered main chain-$\beta(calc.)=18.35$, $\beta(fit.)=18.96\pm1.05$, $\delta^*(cal.)=1.75\cdot10^{-4}$ K^{-1}
- a smectic phase created with an ordered main chain - $\beta(calc.)=22.73$, $\beta(fit.)=23.70\pm1.26$, $\delta^*(cal.)=1.37\cdot10^{-4}$ K^{-1}

The $\beta(cal.)$ value is similar to the $\beta(fit.)$ one. The former was obtained from a DSC experiment, whereas the latter came from DMTA/DETA data. The lack of free volume data for such a system makes the comparison of the $\delta^*(cal.)$ and $\delta^*(exp.)$ impossible. However, the high value of $\beta(cal.)$ and $T_t=317K$ suggests the strong influence of the main-chain arrangement on the α relaxation which occurred in this system. This conclusion is supported by the results obtained in other experiments [11,22].

5. Conclusions

The proposed definition of the relaxation time combines the experimental data of different techniques. Using the data from one method, it will be possible to find (or predict) the measurement parameters of other methods, e.g. DSC → DMTA or positron annihilation → DMTA. Furthermore, the value of the β parameter gives some knowledge of the supermolecular structure of the amorphous phase. In order to predict polymer behaviour for engineering applications, it is very important to know which fraction is created by polymer. According to the β value, it will be possible to describe the strength of the influence of the crystal (liquid-crystal) phase on the polymeric amorphous structures, from weak to strong ($2\leq\beta<\infty$). This is quite similar to the classification of the glasses, which recognise fragile and strong glasses. However, the relation proposed in the approach presented here only includes the fitting parameters, which can be compared with the parameters measured in experiments. Moreover, the mathematical formula gives the answer to a question concerning the origin of the α relaxations as described by the relations which are in agreement with the experimental observation. The value of the β parameter would also yield information about the degree of order existing in the amorphous phase, which could be used for the description of material properties. It is tempting to believe that the new formula and the model presented in this paper will advance the theoretical understanding of the molecular mechanism of the α relaxation.

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