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Micromechanics of stress relaxation in amorphous glassy PMMA. Part I. Molecular model for anelastic behaviour

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Abstract

This paper describes the development of a theoretical model for the strength of mechanical relaxation in terms of micromechanics of deformation. Polymethyl methacrylate (PMMA) is used as the model amorphous polymer. The internal molecular rearrangements during relaxation are identified and accounted for by the rotation of specific atomic groups. Voronoi tessellation is used as a method to characterise the nanostructure in amorphous glassy polymer below T_g. A theoretical model is postulated and shown to provide a limited quantitative prediction capacity of the anelastic deformation and the corresponding stress relaxation based on measurable molecular parameters without adjustable factors. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular model; Micromechanics; Stress relaxation

1. Introduction

Anelastic behaviour has been the subject of research and experimentation for many years, and the field is well covered with phenomenological and molecular theories [1–6]. The essential elements of the theories include the definition of the relaxation strength, $\Delta E/E$, and the associated time constant, τ_R. The understanding of physical and chemical parameters for the latter quantity has attracted most attention through molecular dynamics, atomic bonding and spectroscopy. By contrast, practically no theory exists with predictive powers for the strength of mechanical relaxations in polymers. This view has been expressed strongly in review papers [7,8]. Indeed, there is far more success in predicting the strength of dielectric relaxations in polymers [2,9,10], and in metals, for which many theories have been developed in the past [11–13].

A possibility for new developments based on concepts of conformational structures arose with the improvements in the ability to simulate accurately amorphous polymeric structure [14–16]. In a simulated amorphous cell the nanovolume elements around each side-group or segment can be calculated by Voronoi tessellation and compared to the volume needed for a specific group to move between local minima, and therefore, to relax in a time span comparable to τ_R. This enables one to establish a link between mechanical properties such as the relaxation strength and the nanoscopic structure of amorphous polymers.

The model presented in this paper focuses on quantitative prediction of the magnitude of mechanical relaxation in terms of precisely defined molecular parameters. It is based on rotation of a side-group around an offset bond, resulting in a phenomenon of mass transport and volumetric distortion. Atoms rotate/jump from one position to another within the confined space around the bonded group. This is coupled with a movement of a void space (free volume) in the opposite direction. The net result is a change of shape of the monomer (volume distortion). Although rotation of a side-group leads to a finite translation but no diffusion, multiple rotations of the same side-group are postulated to account for the observed magnitude of relaxation strength. It is in some way analogous to the directional mass flow by diffusion of atoms and vacancies under stress, e.g. the Herring–Nabarro creep in metals [17], or the reversible jumping of small impurity atoms in bcc metals from tetrahedral to octahedral sites, and the associated mechanical relaxation [11,13,18,19].

In this work PMMA is chosen as the model polymer because it has been studied thoroughly in the past, and therefore, it is well characterised. Its molecular chain

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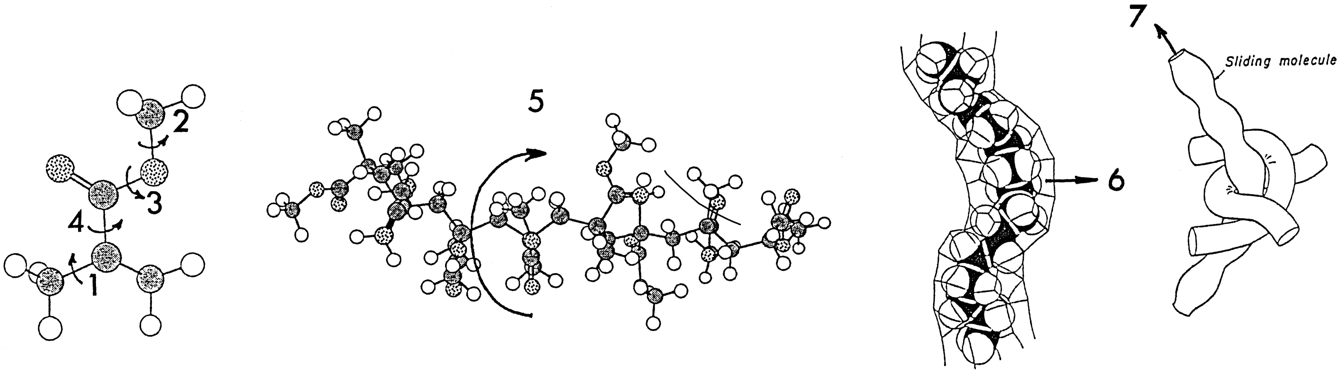

Fig. 1. The seven elementary segmental motions in the molecular chain of PMMA. Motions 1–4 involve atomic groups attached to the chain back-bone. Motion 5 refers to a twisting of a segment of the main chain. Motion 6 involves relative transverse movement between two or more neighbouring chains. Motion 7 involves longitudinal chain movement relative to its neighbours.

architecture allows seven elementary molecular motions of both rotational and translational character as shown in Fig. 1. The molecular motions which give rise to mechanical relaxations in polymers (below the glass transition temperature) have been summarised by Heijboer, and assigned the letters from A to D [4]. In relation to the Heijboer categories, type D is absent (no additives), and type A is further subdivided into three elementary types, AR, ATT and AAT, as listed in Table 1. We concentrate on the first four elementary motions. Each motion contributes to stress relaxation in a polymer sample under load, from small amounts (motions 3 and 4) to significant amounts (motions 1 and 2). A very important effect arises from large variations of individual monomer volumes defined by Voronoi tessellation. It will be shown that these variations of microstructural parameters on nanoscale dimensions can lead to a broad distribution of relaxation times. Quantum effects are neglected so that all atoms have well-defined positions.

2. Theoretical model

2.1. Micromechanics of deformation: the RT event

Consider a polymer in which each monomer contains a side-group of atoms that can rotate around a bond that is not in the backbone of the chain (Fig. 2). Assume the arrangement of atoms to be such that rotation around the bond (by an angle, $\alpha \neq 2\pi$) results in a net displacement of a set of atom(s) from the initial site (1) to another site (2) with an associated voiding of site (1). The net set excludes atoms in the side-group, which possess mirror symmetry in plane containing the axis of rotation. This rotation–translation process will be referred to as an RT event, and the net set of atoms as the NA set. The RT event is the basic element of anelastic relaxation. In this paper, it is assumed that there is no electric or magnetic dipole associated with the monomer. The effects due to the presence of dipoles will be treated in our subsequent publications. To facilitate the description of the model, we represent the monomer in a schematic way as a prism, shown in Fig. 2(b). The monomer is characterised by length, l_0, and Voronoi diameter, Φ, given by:

$$\Phi = \sqrt{\frac{V_{\mathrm{mon}}}{l_0}} \tag{1}$$

The total volume of the monomer (including all its parts) is defined by Voronoi tessellation [20–22], and this volume is denoted by V_{mon}. The Voronoi volume of the side-group attached to the monomer is denoted as V_{sg}, and the Voronoi volume of the NA set as V_{NAS}. The latter is a subset/segment of the total monomer volume, such that $V_{\mathrm{NAS}} < V_{\mathrm{sg}} < V_{\mathrm{mon}}$. The NA set is characterised by the dimensions a and l_{NAS}, such that $a \times l_{\mathrm{NAS}} \times l_0 = V_{\mathrm{NAS}}$. An RT event has the effect of distorting the shape of the monomer. It is postulated that this deformation is described to a good

Table 1
Elementary molecular motions in pure PMMA leading to stress relaxation

	Molecular groups in PMMA	Motion type	Heijboer designation [4]
1	C–COO–CH_3 side-group	Side-group rotation about the bond linking it to the main chain	B
2	CO–CH_3 on the side-group	Rotation of a portion of the side-group	C
3	CH_3 on the side-group	Rotation of a portion of the side-group	C
4	CH_3 on the main chain	Side-group rotation about the bond linking it to the main chain	B
5	Main chain segment	Twist rotation motion of the main chain	ATR
6	Main chain segment	Transverse translation of the main chain segment	ATT
7	Main chain segment	Axial translation of the main chain segment	AAT

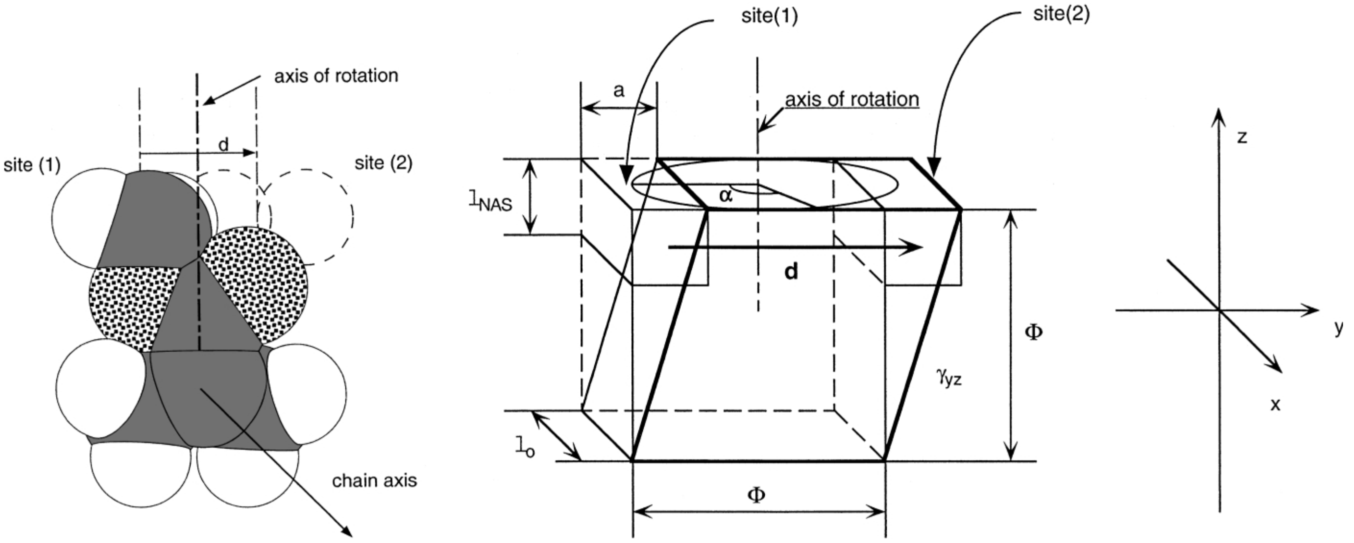

Fig. 2. Rotation of the COOCH$_3$ side-group on the PMMA monomer: (i) on the left a molecular model (to scale), with the main chain axis coming out of the page; (ii) in the centre a schematic representation of the monomer and its changing shape due to side-group rotation/translation; (iii) on the right, a set of local reference axes (chain axis is along the x-direction).

approximation by the following relationship

$$\gamma_{\text{eff}} = \frac{l_0 l_{\text{NAS}} a}{l_0 \Phi^2}\,\frac{d}{\Phi} = \frac{V_{\text{NAS}}}{V_{\text{mon}}}\,\frac{d}{\Phi} \tag{2}$$

where γ_{eff} is effective shear strain of the monomer volume expressed in the local frame of reference, $[xyz]$, and $d = |\mathbf{d}|$ is the magnitude of the displacement vector of the NA-set. The deformation is not homogeneous; it involves a portion of the volume of the monomer, namely V_{NAS}, being moved from one position (site 1) to another position (site 2) without moving the rest of the monomer. The equation is expressed in terms of desired parameters that characterise the molecular elements obtainable from molecular simulations and by Voronoi tessellation method, as described later.

Eq. (2) provides the basis for a convenient relationship to predict the (internal) anelastic strain, expressed in readily measured molecular terms, and overcomes the rather simplistic dimensional features of the monomer as represented in Fig. 2.

Next, we chose another frame of reference, [123], oriented with respect to the $[xyz]$ frame of reference in such a way that the angle between z-axis and 3-axis is Θ. Using strain transformation rules we calculate the normal strain component, resolved along the 3-axis, as:

$$\Delta\varepsilon_3' = \tfrac{1}{2}\gamma_{\text{eff}}\sin 2\Theta \tag{3}$$

The factor 1/2 appears as a result of shear to normal strain transformation [23]. The symbol, Δ, signifies the fact that the strain is an 'internal' strain, representing the rearrangement of atoms within the volume of the polymer, and $(')$ indicates that the strain increment comes from one RT event only. The RT event is an elaboration of a well-established concept for mechanical relaxation via a two-site jump process [5].

The physical manifestation of the RT molecular process will occur as a consequence of disturbance of mechanical equilibrium. In the case of stress relaxation, the phenomenon will be activated by the applied strain, $\varepsilon_{\text{appl}}$, and the uniaxial magnitude of the effect, within the bounds of linear viscoelastic behaviour, will be given by:

$$\Delta\varepsilon(t) = \sum_{i=1}^{N}(\Delta\varepsilon_3')_i C_N \varepsilon_{\text{appl}} = \lambda(t)\varepsilon_{\text{appl}} \tag{4}$$

A polymer sample of volume V contains N number of monomers. In the case considered here, the concentration, C_N, expressed as the number of RT groups per monomer, is equal to one. The quantity, $\Delta\varepsilon(t)$, and its relative measure, $\lambda(t)$, describe the internal molecular re-arrangement occurring in the polymer at $\varepsilon_{\text{appl}} = \text{const} \neq 0$. The subscript (3) is omitted for the uniaxial case, and time dependence derives from the stochastic and kinetic nature of the RT events. The summation in Eq. (4) is carried over all the monomers in the whole volume of the polymer sample. The relevant parameters for the RT event will vary from monomer to monomer, and the summation must be carried out in full. In practical terms, however, we calculate appropriate average quantities for each of the molecular parameters:

$$\lambda(t) = \frac{1}{2}\,\frac{\bar{d}}{\bar{\Phi}}\,\frac{\bar{V}_{\text{NAS}}}{\bar{V}_{\text{mon}}}\sum(\sin 2\Theta)_i \tag{5}$$

For very large N we may approximate the summation by Gauss' theorem:

$$\sum(\sin 2\Theta)_i = \int_0^{2\pi}\int_0^{\pi/2}\sin(2\Theta)\,\mathrm{d}\Theta\,\mathrm{d}\phi \tag{6}$$

We note that:

if *all* monomers are oriented exactly in the same way ($\Theta = 45°$, $\phi = 0°$), *all* side-groups are in the same initial positions, and *all* groups do RT event to the new site by 180° rotation, then

$$\lambda(\max) = \frac{1}{2}\frac{\bar{d}}{\bar{\Phi}}\frac{\bar{V}_{\mathrm{NAS}}}{\bar{V}_{\mathrm{mon}}} \tag{7}$$

which defines the upper bound on the magnitude of the molecular strain parameter caused by one type of side-group rotation in an ideal volume of polymer, if the orientation of the monomers is randomly distributed in space, but in such a way that $0° \le \Theta \le \pi/2$, and $0° \le \phi \le 2\pi$, then the strain parameter will amount to

$$\lambda(\mathrm{random}) = \frac{1}{\pi}\frac{\bar{d}}{\bar{\Phi}}\frac{\bar{V}_{\mathrm{NAS}}}{\bar{V}_{\mathrm{mon}}} \tag{8}$$

if the orientation of the monomers is random in space, $0° \le \Theta \le \pi/2$, and $0° \le \phi \le 2\pi$, and *all* groups do RT event, and the applied strain is zero, then

$$\lambda(\min) = 0 \tag{9}$$

The last case represents the situation in a real sample in a state of mechanical and thermal equilibrium in which rotations of side-groups are thermally activated and occur spontaneously and incessantly without causing any macroscopic deformation or position fluctuation of the polymer volume.

2.2. Continuum mechanics of relaxation

Consider now a polymer sample in the shape of a prism of length, L, and cross-section, A, forced to extend step-wise by ΔL at time $t = 0$. If the polymer behaviour is purely elastic, then the applied force, P, is linearly related to the extension through the tensile modulus of elasticity and the dimensions of the specimen:

$$P = E\left(\frac{A}{L}\right)\Delta L \tag{10}$$

However, if relaxation events are allowed to occur, then at a given extension, ΔL, the force will be diminished with time, t, by some value, $\Delta P(t)$, due to internal stress relaxation by molecular reorganisation, so that the relationship can now be written as:

$$[P - \Delta P(t)] = E_{\mathrm{relax}}(t)\left(\frac{A}{L}\right)\Delta L \tag{11}$$

Thus the effective stiffness of the sample, $[P - \Delta P(t)]/\Delta L$, decreases with time due to the action of the anelastic events. $E_{\mathrm{relax}}(t)$ represents the diminished value of the corresponding tensile modulus at time t. We assume that every RT event causes/allows local stress relaxation on a microscopic scale in the vicinity of the rotated side-group. The sum of all events manifests itself as relaxation at the macro level, so that we may write for the relaxation modulus

$$E_{\mathrm{relax}}(t) = E_{\mathrm{U}}\left\lfloor 1 - \frac{\Delta E(t)}{E_{\mathrm{U}}}\right\rfloor \tag{12}$$

where $E_{\mathrm{U}} = PL/A\Delta L$ is the unrelaxed value of the stress relaxation modulus, $\Delta E(t) = \Delta P(t)L/A\Delta L$, $E(t) = E_{\mathrm{R}}$ for $t \to \infty$ and E_{R} is the relaxed value of the stress relaxation modulus. The link between micromechanics of Eq. (8) and continuum mechanics of Eq. (12) is expressed as follows:

$$\Delta E(t) = \lambda(t)E_{\mathrm{U}} \tag{13}$$

Strict conditions apply to the quantity $\lambda(t)$. It must be equal to zero when temperature is absolute zero ($T = 0$ K), and its maximum value cannot exceed that of the applied strain, $\varepsilon_{\mathrm{appl}} = \Delta L/L$. Thus,

$$0 \le \lambda(t) \le \varepsilon_{\mathrm{appl}}, \qquad \text{for all } 0 \le t \le \infty \tag{14}$$

It follows that $\Delta E \equiv 0$, if $\varepsilon_{\mathrm{appl}} = 0$, and/or if $T = 0$ K. Also, for complete stress relaxation, $\Delta E = E_{\mathrm{U}}$; the polymer behaves as a viscoelastic liquid. By definition [24,25], in a viscoelastic solid, for $t \to \infty$, $\Delta E(t) \to E_{\mathrm{R}} < E_{\mathrm{U}}$. With the above conditions and restrictions, and if only one RT event is allowed to occur per side-group, then the maximum value of the relaxation strength due to that particular RT mechanism is given by:

$$\left(\frac{\Delta E}{E_{\mathrm{U}}}\right)_{\max} = \frac{1}{\pi}\frac{\bar{d}}{\bar{\Phi}}\frac{\bar{V}_{\mathrm{NAS}}}{\bar{V}_{\mathrm{mon}}} \tag{15}$$

The presumption that RT events will result in stress relaxation must now be proven. Thus, it is necessary to establish that RT events will occur when activated by the action of the external deformation of the polymer sample. We consider a mechanism, which puts bias on the RT events during externally applied deformation to give non-zero anelastic flow and stress relaxation.

2.3. Physical criteria for RT events

A physically sound criterion for specifying the necessary condition for an RT event to occur can be constructed on the basis of an assumption that the monomer shear occurs if and when the associated 'internal' strain contributes in a positive sense to the macroscopic stress relaxation suffered by the sample. In mathematical terms, this necessary condition can be expressed in terms of projection of the displacement vector, $\mathbf{d}$, onto the elongation vector, $\mathbf{\Delta L}$. Let $\mathbf{\Delta L}$ be a unit vector aligned in the positive direction of the 3-axis. Then we require that the projection of $\mathbf{d}$ on $\mathbf{\Delta L}$ must have the same direction as $\mathbf{\Delta L}$.

$$\mathrm{Proj}_{\mathbf{\Delta L}}\mathbf{d} = \left(\frac{\mathbf{d}\cdot\mathbf{\Delta L}}{|\mathbf{\Delta L}|}\right)\times\left(\frac{\mathbf{\Delta L}}{|\mathbf{\Delta L}|}\right) > 0 \tag{16}$$

Since $\mathbf{\Delta L}$ is positive by definition, Eq. (16) is always satisfied when:

$$\mathbf{d}\cdot\mathbf{\Delta L} > 0 \tag{17}$$

This criterion provides the necessary condition for the RT process to occur under the influence of the external loading. We note at once that this condition will be satisfied for only a (1/2) fraction of all the monomers in the initial stage of deformation (by virtue of the random spatial distribution, the other half will be in sites not favoured for the transition, i.e. $\mathbf{d}\cdot\Delta\mathbf{L} < 0$). This is equivalent to restricting the limits of integration in Eq. (6) over the angle Θ from -45 to $+45°$. The above criterion is consistent with the second law of thermodynamics. The work of deformation of the sample becomes the Helmholz free energy, and the relaxation of the stress ensures that Clausius–Duhem inequality is satisfied [25]. If the stress tensor is split into two parts according to the scheme

$$\sigma_{ij} = \sigma_{ij}^{(\mathrm{C})} + \sigma_{ij}^{(\mathrm{D})} \tag{18}$$

where the first part is a *conservative* stress tensor, and the second part is a *dissipative* stress tensor, then

$$\frac{\mathrm{d}u}{\mathrm{d}t} = \frac{1}{\rho}\sigma_{ij}^{(\mathrm{C})}\dot{\varepsilon}_{ij} + \frac{1}{\rho}\sigma_{ij}^{(\mathrm{D})}\dot{\varepsilon}_{ij} + \frac{\mathrm{d}q}{\mathrm{d}t} \tag{19}$$

where u is the specific internal energy (which includes the Helmholtz free energy), the second term on the right-hand side is the rate of energy dissipated per unit mass by the stress, and the last term is the rate of heat flux per unit mass into the continuum.

2.4. Molecular dynamics of the RT event

The rotation of a group of atoms on a polymeric chain (or a monomer) is treated here by the rotational isomeric state theory [26,27]. The occupation of site (1) is denoted by $N_1(t)$, and for site (2) by $N_2(t)$. In the closed system we must have:

$$N = N_1(t) + N_2(t) \tag{20}$$

If $\langle N_i \rangle$ is used to denote time-average, then the transitional state theory gives the rate of reaction as follows

$$\frac{\mathrm{d}\langle N_1\rangle(t)}{\mathrm{d}t} = -k_{(1)\to(2)}\langle N_1\rangle(t) + k_{(2)\to(1)}\langle N_2\rangle(t) \tag{21}$$

where $k(1)\to(2)$ and $k(2)\to(1)$ are the rate constants. The solution of this equation involves and requires, in accordance with standard treatment of thermally activated molecular processes [13], that an RT event be governed by the jump rate

$$\nu = \nu_0 \exp(-U(\varphi)/k_\mathrm{B}T) \tag{22}$$

where ν gives the frequency of the RT event in a chosen monomer, and ν_0, k_B and T have the usual meaning. The free energy function, $U(\varphi)$, includes the intramolecular potential, $V(\varphi)$, plus the Helmholz free energy, $A(\varphi)$, which represent the periodically varying potential field in a Born–Oppenheimer (BO) approximation. The usual quasiharmonic approximation [28] allows $U(\varphi)$ and phonon frequencies, ω, to depend on volume but not explicitly on temperature. On the basis of the above assumptions, we obtain the relaxation time constant of the RT process as:

$$\tau_\mathrm{R} = \tau_0 \exp(E_\mathrm{barrier}/k_\mathrm{B}T) \tag{23}$$

We assume the activation energy barrier to have two components [29]:

$$E_\mathrm{barrier} = Q_1 + Q_2(V_\mathrm{v}) \tag{24}$$

Q_1 is the fundamental component due to rotational stearic hindrance alone imposed by the atoms adjacent to the monomer. Q_2 is due to hindrance to rotation arising from the presence of other surrounding atoms/monomers within the polymer, and V_v is a generic symbol for Voronoi volumes of any atom or atomic group. Therefore, the Q_1 component is essentially constant and equal to the activation barrier obtained by theoretical calculations for a chain in free space, by computer simulations, or by appropriate experimental measurements (for example, in polymer solution). On the other hand, the Q_2 component is dependent on the volume available to the monomer (or more precisely, on the Voronoi volume associated with the side-group). Here we choose to measure this volume by Voronoi tessellation [20]. This volume is dependent on several factors such as the polymer thermal history, its present density, presence of void space for the side-group to rotate to, as well as volume dilatation (hydrostatic tension or compression) imposed by the macroscopic extension of the sample. As a first approximation, we represent all of the above factors by a single dependence of Q_2 on Voronoi volume of the relevant side-group, as described by the equations below

$$E_\mathrm{barrier} = Q_1 + \frac{q_2}{x} \tag{25}$$

where x, represents a nanostructural parameter, defined by:

$$x = \frac{V_\mathrm{mon} - V_0}{V_0} \tag{26}$$

In Eqs. (25) and (26) Q_1, q_2 and V_0 are specific constants determined from molecular structural parameters by methods discussed later. V_0 is the volume, V_mon, reduced by thermal contraction to temperature, $T = 0$ K. The values of the parameter x (which describes the variation of the monomer Voronoi volume) can be obtained on the basis of experimental and/or computer simulation studies.

2.5. Structural dependence of the relaxation strength

In a volume of polymer in which there is a significant, but not a very large number of monomers, the Voronoi volumes associated with each side-group of interest can be best represented by a discrete distribution function, $p(V_\mathrm{v})$, with a suitable choice of volume intervals. The distribution contains structural information about that particular volume of polymer. In an amorphous polymer the random packing will result in a finite width of the distribution, such that $V_0 \le V_\mathrm{v}(\min) \le V_\mathrm{v}(\max) \ll \infty$. The width of the distribution will also reflect the condition of the polymer, for example, it will be different for quenched or annealed state. This information can be coded into the relaxation strength by transformation of the distribution into a relaxation spectrum as follows:

$$p_i(V_\mathrm{v}) \rightarrow p_i(x) \rightarrow p_i(\tau_\mathrm{R}) \tag{27}$$

Eq. (26) is used for the first transformation, and Eq. (23) is used for the second transformation. In the above process, p represents the number fraction of monomers, normalised in such a way that:

$$\sum p_i(V_\mathrm{v}) = \sum p_i(x) = \sum p_i(\tau_\mathrm{R}) = 1 \tag{28}$$

In these terms, the time and temperature dependent (and now structure dependent) relaxation strength is given by:

$$\left(\frac{\Delta E}{E_\mathrm{U}}\right)_{(t,T,x)} = \left(\frac{\Delta E}{E_\mathrm{U}}\right)_{\max} \sum_{i=1}^{N} p_i(\tau_\mathrm{R})\left[1 - \exp\left(-\frac{t}{(\tau_\mathrm{R})_i}\right)\right] \tag{29}$$

Updating Eq. (12) with Eq. (29) gives the final relationship for the stress relaxation modulus, showing direct dependence on time and temperature, and the structure of the polymer through the distribution of monomer Voronoi volumes:

$$E_\mathrm{relax}(t,T,x) = E_\mathrm{U}\left[1 - \left(\frac{\Delta E}{E_\mathrm{U}}\right)_{(t,T,x)}\right] \tag{30}$$

As expected, the above relationship is consistent with standard theories of viscoelasticity [1,24,30,31]. If the relaxation spectrum can be described by a continuous analytical function, then the relaxation modulus can be represented by the hereditary integral:

$$E_\mathrm{relax}(t,T,x) = E_\mathrm{R} + \int_{-\infty}^{+\infty} H(\tau_\mathrm{R})\exp\left(-\frac{t}{(\tau_\mathrm{R})}\right)\mathrm{d}\ln(\tau) \tag{31}$$

The point is stressed again that the relaxation strength and relaxation times are functions of the nanostructure of the amorphous polymer through the parameter, x.

2.6. Density dependence of the unrelaxed modulus

There is an indirect dependence of the modulus of elasticity on temperature, which has nothing to do with relaxation processes. It is simply an effect due to variation of density by thermal expansion increasing intermolecular distances, thus diminishing the value of the modulus with temperature [32]. Theoretical prediction of this variation for fcc metals is [33]

$$E(T) = E_0\frac{\rho(T)}{\rho_0} \tag{32}$$

where ρ_0 is the density of the polymer at some reference temperature (say 0 K), and $\rho_0(T)$ is the density at temperature T. This has been derived on the basis that the interatomic separation must increase with temperature in proportion to the linear coefficient of thermal expansion. No such detailed theoretical derivations have been made for amorphous polymers, although it has been reasoned that in polymers density variation with temperature must be accounted for by interchain separation only [34]. Nevertheless, phenomenologically, the variation of density in terms of the macroscopic linear coefficient of thermal expansion, α, must follow a similar relationship as above. Therefore, we assume that to a good approximation the temperature dependence of the unrelaxed modulus of an amorphous polymer is given by:

$$E(T) = \frac{E_\mathrm{U}(0)}{(1+\alpha\Delta T)^3} \tag{33}$$

$E_\mathrm{U}(0)$ is the value of the modulus at 0 K, and ΔT is the change in temperature. The former quantity is not easily accessible by experiment. At best, we make measurements at various temperatures and extrapolate. For PMMA there is also a theoretical prediction for this value, amounting approximately to 3 GPa [35]. This quantity can be also obtained from computer simulations [36].

3. Discussion

3.1. Relaxation strength

Eq. (15) predicts relaxation strength of finite magnitude. This is consistent with the fact that rotation of side-groups can only result in partial (and finite) relaxation of applied stress. A significant feature of this model is that it predicts the strength of mechanical relaxations a priori. The magnitude of the internal shear strain can be calculated with a reasonable degree of confidence in terms of mean values of the characteristic molecular parameters. The only requirement is the detailed knowledge of molecular chemistry and the associated physical nanostructure, which can be described and quantified by the Voronoi method. If this is known, then relatively simple calculations yield the maximum value of stress relaxation due to rotations of the accounted side-groups. To predict the time to reach that relaxation level is a separate matter, and requires the activation energies of the individual molecular motions.

The effect of concentration of side-groups in the polymer has not been considered in any detail. However, it is clear that we are dealing here with high volume fractions (not a dilute case). One may comment to say that cooperative effects will affect the relaxation times of the RT processes, but should not alter the relaxation strength.

It is appropriate to recall the theory of Nowick and Heller [18], and to compare it with the model presented here. The N–H theory is for anelastic relaxations due to defect rotations in crystalline solids. It is of general validity for all materials, and should in principle apply to amorphous glassy polymers, as well. It assumes homogeneous external fields and low defect concentrations so that defect transition has negligible effect on free energy of the crystal. Defects that are present in different but equivalent orientations will produce anelastic strain, $\varepsilon_{ij}^{\mathrm{an}}$, given by

$$\varepsilon_{ij}^{\mathrm{an}} = \sum_{p} \lambda_{ij}^{p} C_p \tag{34}$$

where $C_p = N_p v_p$ is the concentration of defects in terms of mole fraction, and λ_{ij}^{p} is a second order symmetric tensor described by an ellipsoid dipole. The analogy of this equation with the mechanics presented in Section 2.1 is direct. Quantitative adaptation of the N–H theory to amorphous polymers, however, is not straightforward as symmetry operation cannot be identified in amorphous materials by the usual point group methodology [37]. Rather than considering the symmetry operations literally, we recognise that the more general criterion (given above in Eq. (16), combined with the statistical nature of the RT event, ensures that anelastic processes take place.

In deformation of solids with non-directional atomic bonding (for example, metals), the rotational component is neglected, as it has no effect on the behaviour of the material. Rotations of atoms around bonds do not alter the symmetry elements of the crystal, and therefore, are of no consequence to atomic transitions. By contrast, in solids with directional bonding involving two or more atoms (ionic, covalent) rotations can no longer be neglected. This was well recognised in the mechanics of polymer deformations [38], and also in the development of this model.

3.2. Relaxation times and spectra

Previously published molecular theories, which predict distribution of relaxation times for polymers, fall broadly into two categories: (i) theories based on the Rouse bead-and-spring representation of a real polymer molecule (segmental motion type 6, Fig. 1), and (ii) the de Gene reptation theory (elementary motion type 7, Fig. 1). They treat the main relaxation modes of polymer chains, to which the RT model is a complementary mechanism. The side-group rotation RT theory is, therefore, in a separate category.

There is a substantial variation of Voronoi volumes of the monomers and side-groups along each molecular chain, indicating significant density fluctuations on nanoscopic scale. This variation was found in many simulated polymers, it has theoretical foundations [34,39], and supporting experimental evidence [40], and it may be considered to be representative of the true state of nanodensity variations in real amorphous polymers.

In the theory presented here, the distribution of relaxation times is derived from the discrete distribution function, $p(V_{\mathrm{v}})$, which in turn is obtained from the measurements of Voronoi polyhedra for all relevant atoms. The essence of that transformation is contained in the relationship expressed in Eqs. (24)–(26). Whereas Eq. (24) has sound physical basis, Eq. (26) is purely empirical at this stage, and should be considered as the least established element of the RT model, as we have no theoretical justification for its form. Nevertheless, it displays the correct functional form. Note that $E_{\mathrm{barrier}} \to \infty$ as $V_{\mathrm{mon}} \to V_0$. By definition, V_0 is the Voronoi volume of a side-group, which is so small that molecular transition is prevented, except at $T \to \infty$. It is proposed that V_0 is derived empirically by extrapolating to absolute zero temperature. On the other hand, $E_{\mathrm{barrier}} \to Q_1$ when V_{mon} increases (for example, by thermal expansion) towards V_1 which is the Voronoi monomer volume corresponding to the polymer well above its glass transition temperature (liquid state). Similarly, q_2 must be obtained from experimental data involving solution studies. Both quantities as yet lack precise definition, and therefore, are adjustable to some extent, until a satisfactory theoretical treatment is carried out. The distribution of relaxation times for every RT mechanism is broad, ranging from a minimum value, $\tau_{\mathrm{R}}(\min) = \tau_0 \exp(Q_1/k_{\mathrm{B}}T)$, to infinity when, $x = 0$. This feature, together with the finite value of the relaxation strength, categorises the RT model as that of a viscoelastic solid.

The relaxation time of a rotating methyl group in PMMA has been modelled by Nicholson and Davies [41], and measured experimentally by Arrighi et al. [42]. They observed that the distribution of barrier energies is the main origin for the distribution in jumping rates, hence relaxation times. The distribution is asymmetric and broadens with increasing hydrostatic pressure. We concur with their main conclusion that the primary effect of the presence of other molecules in the condensed system is to broaden the range of conformational barriers to rotation. We propose to extend this conclusion to the rotation of other atomic sets. Indeed, the distribution of rotational barriers of the ester set has been modelled and measured by Lousteau [43] and found to be asymmetric, and described to a good approximation by a Γ-function.

3.3. Structure dependence

The results of simulations carried out by the authors using MSI software [44] (to be presented in a subsequent publication) show that the distribution of monomer Voronoi volumes can be described to a good approximation by a generalised Poisson distribution (GPD). Previous calculations carried out on amorphous polymers also give results consistent with the above proposition [45–47]. Similar results for inorganic glasses were published by Tsumuraya et al. [48].

Theory of crystallography defines ideal crystal structure(s) based on the atomic motif and translational symmetry as its fundamental operational elements, subsequently from which space lattice(s) and unit cell(s) are derived. The structures of real materials depart in many ways from the ideal, hence the theories of crystal defects, disorder, and representative volume element. It is frequently tacitly assumed that amorphous materials are found at the limits of disorder. In fact, and especially so for polymers, amorphicity is usually defined by what it is *not* (i.e. no crystalline peaks in XRS, no bond correlation in nuclear magnetic resonance (NMR)), rather than by what it *is*. The lack of a specific definition inhibits complete understanding of amorphous materials. A theoretical development of ideal amorphous structures is required to provide firm foundation for the correlation of molecular structure with properties and behaviour, especially where there is need to describe relative motions and non-conservative transitions of atoms or atomic groups [19]. The geometric system based on Voronoi space tessellation possesses these properties, and has the potential to represent the static structure well, in the same way as crystallography describes the static structure of crystalline solids.

External actions, such as temperature, quenching and annealing, pressure, and mechanical deformation will alter the structure of the polymer, and therefore, affect the distribution of Voronoi volumes. For example, the distribution of Voronoi volumes for (i) a quenched, and (ii) an annealed polymer will differ in a measurable way. Although there is no direct experimental method to measure the Voronoi volumes in a polymer, the distribution can be derived from X-ray scattering. If Φ_V is the distribution, then for an isotropic sample the scattered intensity will be given by the standard formula:

$$I(s) = \frac{Nf^2}{V}\left[1 + \frac{1}{V}\int_0^\infty (\Phi_V(r) - 1)4\pi r^2 \frac{\sin(2\pi rs)}{2\pi rs}\,dr\right] \quad (35)$$

The relationship between the distribution of Voronoi volumes and the radial distribution function was established for simple monoatomic structures by Finney [49]. An elaboration of the structure and properties of amorphous polymers will be published later.

4. Conclusions

The character of molecular motions responsible for mechanical relaxations in polymers below the glass transition temperature has been elaborated on. In particular, the theoretical treatment of relaxation associated with side-group motion provides a clear model for relating the phenomenon to molecular quantities.

The inadequacy of available theories and mathematical models, expressed in the published literature, has been diminished, and the field has been ameliorated with a self-consistent theory, which is firmly based on molecular structure of the amorphous polymer.

The RT model can be applied in general to all polymers with side-groups, which can rotate or transform from one to another site and configuration.

The description of molecular motions responsible for mechanical relaxations has been elaborated on beyond the original Heijboer classification to reveal their contribution to the strength of mechanical relaxation.

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