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Course Notes of Chapter 4.2 (Part 2)

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1. Introduction: Molecular Approach to Viscoelasticity

1.1 The Physical Origin of Viscoelasticity

In our course on linear viscoelasticity, we used phenomenological models so far (springs, dashpots) which have no direct link with what we know already on the physics of polymers, namely that they are generally made up of more or less flexible molecular chains. On the other hand, **we have already established that an elastomer, i.e. a lightly crosslinked flexible polymer deformed at a temperature above its T_g behaves like an "entropic" spring** with a Young's modulus

$$E = 3NkT$$

where N is the density of crosslinking points. **We also got a phenomenological description of linear behavior (with small strains) above the glass transition** according to which the modulus of relaxation, for example, is given by

$$\mathrm{E}(t) = E_\infty + \sum_{1}^{n} E_i e^{-\frac{t}{\tau_i}}$$

where τ_i are "relaxation times" and E_i are arbitrary constants, which can be adjusted to reproduce the observed behavior. In the case of an elastomer, we can assume that $t \gg \tau_i$ and that $\mathrm{E}(t) \longrightarrow E_\infty$. Thus, by comparing the two expressions above, $E_\infty = 3NkT$. We can rewrite the above equation as follows:

$$\frac{\mathrm{E}(t,T)}{3NkT} = 1 + \sum_{1}^{n} \alpha_i e^{-\frac{t}{\tau_i(T)}}$$

$$\frac{\rho_2 T_2 \mathrm{E}(t_1,T_1)}{\rho_1 T_1} = \mathrm{E}_r(t_1,T_1) = \mathrm{E}(t_2,T_2)\left(\sum_{0}^{n} \alpha_i e^{-\frac{t_1}{\tau_i(T_1)}} \Big/ \sum_{0}^{n} \alpha_i e^{-\frac{t_2}{\tau_i(T_2)}}\right)$$

with $\alpha_0 = 1$ and $\tau_0(T_1) = \infty$. If all τ_i show the same dependence with T, we can replace them by $\tau_{i0} f(T)$:

$$\mathrm{E}_r(t_1,T_1) = \mathrm{E}(t_2,T_2)\left(\sum_{0}^{n} \alpha_i e^{-\frac{t_1}{\tau_{i0} f(T_1)}} \Big/ \sum_{0}^{n} \alpha_i e^{-\frac{t_2}{\tau_{i0} f(T_2)}}\right)$$

Thus, if we know $f(T)$, the τ_{i0}, the α_i and $\mathrm{E}(t_2, T_2)$, we can calculate $\mathrm{E}_r(t_1, T_1)$ and therefore $\mathrm{E}(t_1, T_1)$ for any values of t_1 and T_1. This is the principle of **time-temperature superposition**,[1] and as long as we stay in the temperature window immediately above T_g, we can use the WLF equation to obtain $f(T)$. This equation has the advantage of being supported by the theory of free volume or at least by observations of the change in viscosity near T_g.

On the other hand, **one does not know yet how to connect $\boldsymbol{\tau_{io}}$ and $\boldsymbol{a_i}$ to the structure of the chains.** In addition, in a non-crosslinked polymer (a thermoplastic), there is a rubbery plateau which is limited in temperature and time, i.e. that $\tau_0(T)$ has a finite value. **How do you explain the existence of a rubbery plateau in the absence of crosslinking points**?

1.2 Entanglement

The answer to the last question in section 1.1 is "**entanglement**". So far, we have referred to entanglement in rather vague terms, sometimes saying that the chains of a molten polymer must be strongly "entangled" and are significantly constricted due to the presence of other chains. We could therefore imagine that these constraints play the same role as the chemical crosslinks in a conventional elastomer, which would explain the existence of the rubbery

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[1] (In other words, $\mathrm{E}_r(t_1, T_1) = \mathrm{E}(t_2, T_2)$, i.e. we have the same behavior, when $t_1/f(T_1) = t_2/f(T_2) = t_{\mathrm{ref}}/f(T_{\mathrm{ref}}) \Longrightarrow t_1/t_{\mathrm{ref}} = a_T(T_1, T_{\mathrm{ref}})$, or, in the frequency domain, $\omega_{\mathrm{ref}}/\omega = a_T(T, T_{\mathrm{ref}})$. (For recall, if $T > T_{\mathrm{ref}}$, $\log a_T(T, T_{\mathrm{ref}}) < 1$ according to the equation of WLF and the curves of $\mathrm{E}_r(t)$ are shifted towards shorter times than at T_{ref}, while the curves of $\mathrm{E}_r(\omega)$ are shifted to higher frequencies higher than T_{ref})

plateau. But can we find a more precise description of this phenomenon that will allow us to quantify the effect of entanglement on the mechanical behavior of a polymer and to relate it to the structure of the polymer?

1.3 Disentanglement?

As it was mentioned at the end of 1.1, the rubbery plateau has a limited extent in temperature or time, and the effective value of $\tau_0(T)$ is therefore not infinite for a thermoplastic. Thus, if a chain can be entangled with its neighbors, it can also become “**unentangled**” if its mobility is high enough or if given enough time. This disentanglement is often described in terms of "**reptation**", a word that evokes the movement of a snake (or reptile) which tries to squeeze between obstacles. There too, we would like to find an accurate description of this phenomenon in terms of the polymer structure and, in particular, of its molar mass, since we already know that the observed extent of the plateau depends strongly on M.

2. Isolated Chain Dynamics in a Solvent: the Rouse Model

2.1 Isolated Chains in a Solvent

The viscoelastic behavior of a very dilute solution is expected to reflect the dynamics of an isolated chain as long as it interacts with the solvent. Rouse proposed the following simplification: We consider a freely jointed chain containing n bonds divided into m - 1 “subchains” of identical length, connected by m “balls”, which interact with the solvent. If the subchains are long enough, they will have a Gaussian behavior and therefore a mean square distance between ends

$$R_s^2 = \frac{n}{m-1} l^2 \tag{1}$$

If the ends of a given subchain are defined by the vectors $\vec{r}_i$ and $\vec{r}_{i+1}$, the force of contraction acting along the vector $\vec{r}_{i+1} - \vec{r}_i$ is given by

$$f = \frac{3kT}{R_s^2}(\vec{r}_{i+1} - \vec{r}_i) \tag{2}$$

The force on the ball located at $\bar{r}_i$ must be in equilibrium with the viscous forces acting on this ball:

$$f = \frac{3kT}{R_n^2}(\vec{r}_i - \vec{r}_{i-1}) + \frac{3kT}{R_n^2}(\vec{r}_{i+1} - \vec{r}_i) = -\xi\frac{d\vec{r}_i}{dt} = \frac{3kT}{R_n^2}(2\vec{r}_i - \vec{r}_{i-1} - \vec{r}_{i+1}) \tag{3}$$

where the coefficient ξ is in [Ns/m]. There are m such coupled equations for the entire chain. In order to solve them one carries out a "transform of normal coordinates" (see the standard texts) to obtain m independent equations each corresponding to a "mode" of different vibration. Thus, for a solution containing N independent chains per unit of volume:

$$\mathrm{G}(t) = NkT \sum_{p=1}^{m} e^{-\frac{t}{\tau_p}}$$

$$\mathrm{G}'(t) = NkT \sum_{p=1}^{m} \frac{\omega^2\tau_p^2}{1+\omega^2\tau_p^2}$$

$$\mathrm{G}''(t) = NkT \sum_{p=1}^{m} \frac{\omega\tau_p}{1+\omega^2\tau_p^2}$$

$$\tau_p = \frac{\xi R_s^2}{24kT}\sin^{-2}\left(\frac{\pi p}{2(m+1)}\right), \quad p = 1,2\ldots m$$

$$\approx \frac{\xi m^2 R_s^2}{6\pi^2 p^2 kT} \text{ for } m \gg 1, p \tag{4}$$

Here, each p corresponds to a mode of vibration with p nodes along the chain. The longest τ_p therefore corresponds to relatively long chain lengths. We see that:

(i) These equations have the same form as the expressions derived from the **Generalized Voigt-Maxwell model**, except that here all E_i are equal to NkT.

(ii) The dependence of all relaxation times τ_p with the temperature is that of $\xi(T)/kT$.

(iii) The choice of m is arbitrary, as long as $t \gg \tau_m$.

(iv) **The longest relaxation time, τ_1, which involves the whole chain, called the Rouse relaxation time, is proportional to the squared molar mass, M^2,** because $\xi m^2 R_\mathrm{n}^2 = \xi mnl^2 = \xi_0 n^2 l^2 \propto M^2$, where **$\xi_0$ is the "monomeric friction coefficient".**

(v) At the longest frequencies, we find the liquid behavior of the terminal regime of phenomenological models, i.e. G' ~ ω^2 and G" ~ ω.

(vi) At intermediate frequencies, G' ≈ G″ ~ $\omega^{1/2}$.

2.2 Comparison with Experiments

Initially, this model was intended to describe the behavior of a dilute solution. We can do rheological measurements and determine G' and G" and we can also determine the diffusion coefficient of chains, which is given by

$$D_R = \frac{kT}{\xi m} = \frac{kT}{\xi_0 n} \propto \frac{1}{M} \tag{5}$$

according to Rouse's model (see standard texts for development). However, experiments rather show that $D \propto M^{-1/2}$ and $\tau_1 \propto M^{3/2}$. **Rouse's model doesn't work for diluted solutions**. Indeed, we get a better agreement, when we take the influence of the chain on the local speed of the solvent into account, like in Zimm's theory, which we will not consider here.

In contrast, **the Rouse Model is well suited for non-crosslinked polymers above T_g** (where the "solvent" consists of other, relatively small mobile chains), as shown on Slide 276, where we find the same dependence with ω, **provided that**

(i) **The molar mass, M, is not too high**. Otherwise, we observe a rubbery plateau, which is not predicted by the Rouse model.

(ii) **The time (or $1/\omega$) is not too short**, because the Rouse model is not applicable at very short time scales

At the shortest times, the behavior is dominated by the shortest τ_i and therefore the values of p are high according to Equation 4. However, if the number of n/p segments involved in the relaxation becomes too low (typically < 8), we can no longer use Equation 2 and the model is no longer valid.

3. Entanglement and Disentanglement

The Rouse Model is only valid for relatively small M because it does not consider entanglement, i.e. the phenomenon that explains the existence of the rubbery plateau. But what is entanglement?

3.1 Physical Constraints for a Chain in a Condensed Polymer

It is assumed that the chains of an amorphous polymer adopt a Gaussian conformation in the condensed state (molten state, glassy). We did a little calculation for a typical polymer (Slide 282), which establishes that the chains are strongly interpenetrated, i.e. that the volume occupied by a random coil which has a radius of gyration, r_g, contains on average dozens of other chains. If we admit that one chain cannot cross another, we can consider that one given chain is trapped in sort of a "cage" made up from its neighbors (*cf.* Slide 283). We can therefore imagine that the dynamics of each chain are strongly influenced by these constraints, even at temperatures well above T_g where it is assumed that the deformations do not involve a change of internal energy. These constraints must be particularly severe when it comes to cooperative movements involving long chain lengths, that is for the first Rouse modes (p = 1, 2, ...).

3.2 First notions of entanglement: static models

First, we can make an analogy between the rubbery plateau of a non-crosslinked polymer and the modulus of an elastomer, assuming that the constraints on a chain due to its neighbors act as cross-linking points. The process is then very simple: we define an "entanglement density", N_e, according to

$$E_e = 3N_e kT \qquad (6),$$

where E_e is the Young' modulus[2] which corresponds to the rubbery plateau (in fact, the plateau is not perfectly flat but that doesn't matter too much here).

This is the model of the "entanglement network" whereby a non-crosslinked polymer is considered as a network of subchains of average molar mass M_e, called the "mass between entanglements" linked by "entanglement points".

Obviously, if $M < 2M_e = M_c$, the chains are not long enough to constitute a network and, indeed, we do not observe a rubbery plateau under these conditions (using M_e estimated from measurements on very long chains). **M_e is therefore a key parameter, because it marks the threshold of M where the characteristic properties of long chains begin to be manifested**. We will see next week that M_e is very important for the resistance to large deformations, for example, as well as for the behavior in the liquid state (i.e. beyond the rubbery plateau).

M_e and the density of entanglements, N_e, are specific parameters of each type of polymer, but vary greatly depending on the polymer, as shown in the table (cf. Slide 285).

Table 1. Characteristic parameters of common thermoplastics

	Densité (g/cm3)	M_e (g/mol)	C_∞	N_e (mmol/cm^3)
PS	1.05	18700	10.8	0.0561
PMMA	1.17	9200	8.2	0.127
PVC	1.4	5560	7.6	0.252
PA6	1.08	2480	6.2	0.435
POM	1.25	2550	7.5	0.49
PA66	1.07	1990	6.1	0.537
PE	0.85	1390	6.8	0.613
PC	1.2	1790	2.4	0.725
PET	1.33	1630	4.2	0.815

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[2] We can also measure G_e for example, in which case $G_e = N_e kT$.

Establishing correlations between the chemical structure of the polymer and M_e is not as obvious as in the case of T_g and T_m. Nevertheless, we notice that two factors are important, the rigidity of the chain and the number of chains per unit volume. Thus, rigid chains with a low molar mass per catenary bond, M_b, may show a higher entanglement density than flexible chains with a rather high M_b (compare polyethylene and polycarbonate in Table 1). On the other hand, bulky chains, yet not particularly rigid, show low entanglement densities (*cf.* polystyrene). This has led to attempts to establish empirical relationships between M_e, C_∞ and M_b, such that $M_e = 3M_bC_\infty^2$, but the correlations are not strong enough for this kind of equation to be really reliable.

Finally, in the case of an elastomer, entanglements are also present and contribute to the effective crosslinking density as follows

$$N_{eff}^{-1} = N_e^{-1} + N_x^{-1} \qquad (7),$$

where N_x is the density of chemical crosslinks, although we tend to ignore the effect of entanglement in the theory on rubber elasticity.

3.3 Disentanglement: the Tube Model

So far, our static model explains the existence of the rubbery plateau in thermoplastics, but we haven't explained why the extent of this rubbery plateau is limited. At the same time, we can wonder whether the notion of "points" of entanglement has some physical reality. Indeed, we need to give up in considering entanglements like well located "knots" in space. The entanglement network is useful in some contexts, but it is only a static model, and as such it is not very helpful in understanding "disentanglement" at the end of the plateau, which is clearly a dynamic phenomenon.

We will therefore use the idea of a cage formed around a given chain by its neighbors (Slide 288). For a very long chain, this cage takes the form of a tube. The chain cannot pass through the walls of this tube, but if it has some mobility it can escape from the tube at its ends, which remain open. As the tube follows the contour of the chain, its contour length, L, must also be proportional to n, the total number of bonds in the chain, and therefore to M.

Suppose now that we apply a deformation to the polymer and therefore to the tube and that we follow the evolution of the stress (a relaxation test, therefore). To relax the stress after deformation of the tube, a deformed chain must regain its random conformation. However, it cannot pass through the walls of the deformed tube. If the tube has a diameter of d_e, this implies that only chain segment lengths equal or less than d_e can relax, ie. adopt a random conformation. We will now show that d_e corresponds to a length of a chain with mass M_e.

Let's use Rouse's model (Equation 4). *Assuming that the chain gets stuck in the deformed tube*:

$$\mathrm{G}(t) = NkT \sum_{p=1}^{m} e^{-\frac{t}{\tau_p}}$$

$$\begin{cases} \tau_p \approx \dfrac{\xi m^2 R_s^2}{6\pi^2 p^2 kT} \quad \text{for } \dfrac{nl^2}{p} \leq d_e^2 \\ \\ \tau_p = \infty \quad \text{for } \dfrac{nl^2}{p} > d_e^2 \end{cases} \qquad (8).$$

So if:

$$t \gg \tau_e = \frac{\xi m^2 R_s^2}{6\pi^2 kT} \times \frac{d_e^4}{n^2 l^4} = \frac{\xi m d_e^4}{6\pi^2 kTnl^2} = \frac{\xi_0 d_e^4}{6\pi^2 kTl^2} = \frac{\xi_0 l^2}{6\pi^2 kT}\left(\frac{M_e}{M_b}\right)^2 \qquad (9),$$

I.e. in the rubbery plateau:

$$\mathrm{G}(t) = NkT\frac{nl^2}{d_e^2} \equiv N_e kT$$

$$\frac{nl^2}{d_e^2} = \frac{N_e}{N} = \frac{M}{M_e}$$

Thus, **the tube diameter, d_e, is the distance between the ends of a chain with M_e,** and the tube itself is therefore a random chain with a contour length

$$L = \frac{M}{M_e} d_e \qquad (10).$$

However, the chain does not remain blocked in the tube, but leaves the tube after a time τ_d, called the "disentanglement time" or "reptation time". We can obtain a very simple scaling law for τ_d by remembering Equation 5, which tells us that the diffusion coefficient, D, is proportional to $1/M$ according to the Rouse model, and that the length of the tube, L, is proportional to M. According to Fick's law, the diffusion distance by the chain at a time t is

$$x = \sqrt{Dt} \qquad (11).$$

The chains can thus diffuse a distance L and therefore escape from its tube in one step

$$\tau_d \approx \frac{L^2}{D_R} = \frac{\xi_0 n}{kT}\left(\frac{M}{M_e}\right)^2 d_e^2 = 6\pi^2\left(\frac{M}{M_e}\right)^3 \tau_e \qquad (12),$$

where τ_e is the time of the start of the rubbery plateau (Equation 9).[3]

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[3] In the more rigorous treatment of Doi and Edwards, for example, we obtain $\tau_d = 3\left(\frac{M}{M_e}\right)^3 \tau_e$

Once the chain is outside the tube, it can return to its random conformation, and the stress will be completely relaxed. In a simple description, therefore, we can simply replace the Rouse relaxations, which are blocked by the tube, by a term involving τ_d or

$$\mathrm{G}(t) = NkT\left(e^{-\frac{t}{\tau_d}} + \sum_{p=1}^{d_e^2/nl^2} e^{-\frac{t}{\tau_d}}\right) \qquad (13).$$

We can thus summarize the behavior during a relaxation test as shown schematically on Slide 290.

(i) Instant tube and chain deformation (no relaxation, high stress)

(ii) Rapid Rouse-type relaxation inside the tube up to $t = \tau_e$

(iii) Rubbery plateau for $\tau_e < t < \tau_d$

(iv) The chain begins to escape from the tube when $t = \tau_d$ (reptation)

(v) Fully restored random conformation, relaxation terminated when $t >> \tau_d$

We therefore have a complete description of the observed behavior of a non-crosslinked polymer of mass $M > M_e$ in relaxation as well as for an elastomer if τ_d is infinite and d_e corresponds to the effective distance between crosslinking points.

We are not going to discuss other viscoelastic phenomena here, but we have already reproduced important results of the tube theory developed by DeGennes and Doi and Edwards in the 1970s, which provides a fairly complete description of viscoelasticity of polymers above T_g, including the non-linear behavior. The general formulation of this theory is rather complex, but is the basis of many numerical simulations which are widely used in industry for modelling of, for example, the filling of a mold.

What are these important results? First, the time to disentangle (or the reptation time) **τ_d is proportional to M^3, while the time τ_e, which corresponds to the start of the rubbery plateau, depends only on d_e and M_e** (Equation 9). Thus, by **increasing M, one greatly increases the extent of the rubbery plateau.** However, both show the same dependence with temperature and the time temperature superposition can therefore be justified until the transition zone, even in the presence of the rubbery plateau. We also see that **a chain with $M \lesssim M_e$ does not have a rubbery plateau, in accordance with experiments and the network model**.

Other important results, which have been verified by experiments:

Self-Diffusion Coefficient of an Entangled Chain

When the chain leaves its inner tube in the time τ_d, its center of mass moves by an average distance of approximately R_n. According to Fick's law (Equation 11), the self-diffusion coefficient is therefore

$$D = \frac{r_0^2}{\tau_d} \sim \frac{M}{M^3} \sim M^{-2} \qquad (14).$$

Viscosity in the Terminal Zone

In the regime of viscous behavior ($t \gg \tau_d$), the theory of Doi and Edwards predicts that

$$\eta \sim \left(\frac{M}{M_e}\right)^3 ; \quad M > M_c \equiv 2M_e$$

$$\eta \sim \frac{M}{M_e}; \quad M \le M_c \equiv 2M_e \qquad (15).$$

So, there is a change in slope of the η vs. M curve, when M is equal to M_c, which is called the critical molar mass. This is verified for amorphous polymers, and provides a way to obtain M_e for semi-crystalline polymers, where the rubbery plateau is obscured by crystallinity and we cannot measure E_e. In practice, we rather observe $\eta = \eta_0(M_w/M_e)^{3.4}$ when $M_w > M_c$, but this can be explained by the dispersity and the fact that the tube is not completely immutable, as it itself is made up of chains capable to diffuse. What is important, especially for the processing, is that the viscosity is very strongly dependent on the molar mass. So, if the ultra-high molecular weight polyethylene (UHMWPE) is highly praised for its mechanical performance, it cannot be injected because its viscosity is too high. On the other hand, an HDPE of low molar mass is easy to process, but risks to perform in a disappointing manner, particularly in creep.

4. Summary

- Isolated chains may be described using the Rouse model (springs and beads): better agreement with dynamics in dilute solution when hydrodynamic interactions are taken into account (Zimm model)
- For sufficiently long chains in the condensed state, entanglement effects must be taken into account. The existence of a rubbery plateau above T_g for non-crosslinked polymers has led to the idea of the "entanglement network" and M_e. For $M < 2M_e$, entanglement effects are not seen.
- For sufficiently long times and/or at sufficiently high temperatures, entanglements can no longer be considered permanent. General descriptions of viscoelasticity use "tube

models" which allow for disentanglement by reptation. These account for the strong influence of M on the melt viscosity, diffusion etc.