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Relaxation Phenomena in Polymers

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Foreword

It is with particular pleasure that the Society of Plastics Engineers sponsors and endorses "Relaxation Phenomena in Polymers." Its author, Dr. Shiro Matsuoka, embodies the technical excellence which the Society strives to achieve. He was one of the first recipients of SPE's Award in Engineering and Technology and is one of only 90 Fellows of the Society. In addition, he has long served on the Advisory Board of Polymer Engineering and Science.

Most importantly, however, is his membership in the National Academy of Engineering. He is among the few with a background in polymers and plastics elected to this prestigious body. Who then can be better qualified to author this volume, particularly in view of his 35 years of experience in writing and presenting technical dissertations.

SPE, through its Technical Volumes Committee, has long sponsored books on various aspects of plastics and polymers. Its involvement has ranged from identification of needed volumes to recruitment of authors. An ever-present ingredient, however, is review of the final manuscript to insure accuracy of the technical content.

This technical competence pervades all SPE activities, not only in publication of books but also in other activities such as technical conferences and educational programs. In addition, the Society publishes periodicals – *Plastics Engineering, Polymer Engineering and Science, Polymer Processing and Rheology, Journal of Vinyl Technology* and *Polymer Composites* – as well as conference proceedings and other selected publications, all of which are subject to the same rigorous technical review procedure.

The resource of some 37,000 practicing plastics engineers has made SPE the largest organization of its type worldwide. Further information is available from the Society at 14 Fairfield Drive, Brookfield, Connecticut 06804, U.S.A.

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Preface

I have been fortunate to spend thirty years of my career at AT&T Bell Laboratories in close contact with world-class scientists, while keeping in touch with some of the most interesting engineering projects in industry. I recall that the dielectric properties of the ultrapure polyethylene being considered for the transoceanic submarine cable were so critical that we introduced an empirical equation: 10 microradian of $\Delta \tan \delta$ = \$1M of savings in the repeater cost. Aside from such special applications, AT&T was consuming 100 million dollars worth of plastics every year. Even though those times were exciting enough, the use of polymers has taken another dimension since then. Today, the optical fiber cables utilizing all sorts of polymers have replaced the coaxial cables; a miniature ultra-dense computer package with performance comparable to a Cray computer is being tested; the twenty Stealth bombers made of polymer composites have done more than 70% of destruction in the gulf war. The technology has made remarkable progress, and many new applications have emerged, and polymers are more than ever the essential part of new advances in the new technologies.

To predict engineering properties of polymers from their molecular structure is everyone's ambition. There are two main theories that are crucial to the work presented in this book. One is the process of the cooperative conformational relaxation. The basic relaxation rate is determined by the chemical potential of the transition state, but the required simultaneous cooperative relaxation among the neighboring molecular segments reduces the probability of successful relaxation by zth power, where z is the number of the cooperating and interlocked segments. The temperature dependence of the relaxation time does not follow the Arrhenius formula because the number z for the cooperating segments increases with the decreasing temperature, resulting in an enormous (and changing) value for the observed temperature coefficient near T_g. From the model distribution of domain size based on free volume fluctuations, we have obtained an equation for relaxation that fits data better than the Kohlrausch-Williams-Watts equation, especially in the high frequency range that is an important time range for the prediction of the mechanical properties of glassy polymers.

The second crucial theory we have incorporated is the theory of viscoplasticity. Stress is a manifestation of the elastic or stored free energy. The yield phenomenon occurs when the elastic energy exceeds the breaking strength of those domains. However, if strained slowly, the work energy is dissipated through the relaxation process before the yield stress is reached. The behavior, as described above, combines the features of linear viscoelasticity at low stresses and classical plasticity at high stresses; hence, it is termed viscoplasticity (elastico-visco-plasticity might have been more appropriate but cumbersome). Because the fraction that relaxes before reaching the yield (and never goes through yield) depends on the relaxation spectrum at a given strain rate, this apparently nonlinear behavior can be accurately predicted from the linear viscoelastic relaxation spectrum. Prediction of the yield stress at a given strain rate and temperature is possible. We have also shown that the non-Newtonian flow behavior of the polymer melts is in fact the viscoplastic behavior, only different from the solids in the level of the critical levels of stress and strain. Two computer programs have been included in this book with which many kinds of engineering properties can be calculated from the actual stress-strain data.

For the work presented in this book, I owe so much to so many of my friends and colleagues. First and foremost, Xina Quan, who has co-authored some crucial papers that became the basic part of this book, steadfastly declined to allow her name to be used as the co-author, although I feel her contribution was an essential part of this book. Harvey Bair, Ed Johnson and Jim Ryan have been my constant companions for all of the work included here. I have been lucky to have worked closely in the past with Graham Williams (University College of Wales at Swansea), Takeo Furukawa (Institute of Physical and Chemical Research in Tokyo) and Yoichi Ishida (deceased, formerly Kyushu University). Bryce Maxwell (Princeton University), Lee Blyler, and Bob Staats-Westover (retired) have taught me much on polymer engineering. My association with Glenn Frederickson (now at University of California, Santa Barbara) was particularly fruitful, giving me much needed insight to the concept of intermolecular cooperative relaxation. In fact, the molecular model in Chapter 2 can be described with the parameters from the Frederickson-Anderson Ising model. Yasu Koike (Keio University) and Takumi B. Tanaka (UNITIKA) have helped me on many related subjects while undertaking their extended visits at Bell Laboratories. Jehuda Rosenberg

(Israel) and Hany Ghoneim (Rochester Institute of Technology) spent their postdoctoral years at Bell Laboratories, teaching me applied mechanics. I had the world's brightest summer undergraduate program student from Princeton, Jack Hergenrother, who helped me on viscoplasticity of polymer melts. He subsequently went to Cambridge on the Marshall Scholarship, then went on to Harvard to study physics.

And then there is a group of notable names with whom I have spent time at Bell Laboratories: Bill Slichter (deceased), Dave McCall, Dean Douglas, Stretch Winslow, Frank Bovey, Linc Hawkins (retired), Doug Keith (U. Conn), Frank Padden, Andy Lovinger, Dale Pearson (UCSB), Gene Helfand, Henry Wang (Rutgers), Alan Tonelli (NC State U), Gary Patterson (Carnegie-Mellon), T. K. Kwei (Polytech U., NY), Lou Manzione, Reddy Raju, Sanjay Patel, Karl Amundson, Ken Takahashi, Ron Larson, Frank Bates (U. Minnesota), Susan Muller (UCB), Arturo Hale, Faith Morrison (Mich Tech U), Carl Taylor, Charles Aloisio, Paul Kelleher (retired), Phil Hubbauer, and I am sure I missed some names. I owe to names that I can't even begin to cite. I can only make a second-hand quotation from Chris Macosko (U. Minnesota) who quoted Lee Blyler who said, "I would like to thank all those people, whom I neglected to acknowledge over many years, whose original ideas have shaped my thinking and enabled me to make advances in the engineering and technology of plastics ...."

Shiro Matsuoka
Murray Hill, New Jersey
February, 1992

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Stress and Strain

This chapter presents a collection of mathematical tools that will be useful when relating molecular structure to phenomenologically observed behavior. These tools are utilized throughout this volume.

1.1 Free Energy and Stress

The word "potential" is a relative term. On the earth's surface, altitude is a kind of potential. By international agreement, altitude is expressed relative to sea level, but a local altitude might also be expressed relative to a nearby lake. Thus, altitude is a measure of a relative work potential, and potential energy depends on what we decide to be the ground potential.

The same principle of the relative nature of the potential applies to the *free energy* of a material. At 0 °C, 1 mole of gas contained in a 22.4 liter vessel will exert a pressure of 1 atmosphere on the inside wall, and we refer to this thermodynamic state as the standard condition, a sort of zero level potential. If this vessel has a piston, we can increase the pressure to 2 atmospheres by using an external force, and the volume of the gas will be reduced by half. The work performed on the gas is

$$W = \int_{V/2}^{V} p \, dV \qquad (1.1.1)$$

This compressed state has a potential to do work, because when the external force is removed and the pressure is reduced back to 1 atmosphere, the entire amount of work W will be returned by the gas. The gas under a pressure of 2 atmospheres tries to come back to the original standard condition as if it were a compressed spring. The energy that can be returned in this manner is free energy.

A solid material typically behaves like a spring when an external force is applied. In this case the zero energy level state is the state under zero external force. In many hard solid materials, the entire amount of work done by the external force results in a temporary deformation of the material but

the original state always returns when the force is removed. Such materials are called *perfectly elastic*. Although many substances behave nearly perfectly elastically when the deformation is small, they will either fracture or yield when deformed beyond certain limits. The recoverable elastic strain energy is one type of free energy. Its quantity can be calculated in the same manner as the free energy in the compressed gas was calculated above. Let us consider pulling a rectangular bar of length l_0 from both ends. When the force is increased from 0 to F, the length will increase from l_0 to l. The work done, W, is equal to

$$W = \int_{l_0}^{l} F \, dl \tag{1.1.2}$$

For the energy density, i.e., the work per unit volume, the stress σ (the force per unit area) is integrated with respect to the strain ε (the deformation per unit length):

$$\Psi = \int_{0}^{\varepsilon} \sigma \, d\varepsilon \tag{1.1.3}$$

In the discussion above, only the simplest case of uniaxial tension was cited. The stresses vary depending on the choice of the angle of the cross-sectional area, even if the external force remains the same. The stress considered in the example was in the plane perpendicular to the direction of pull. Because of this choice of angle, there were no shear components in the plane. If we now consider a plane inclined 45° from the direction of pull, there will be shear stresses. The free energy in either case nevertheless remains the same, since energy is a scalar quantity. This is a very important principle, meaning that the total of all stress components at a point depends only on the boundary condition. It also means that if the stresses are known for three orthogonal planes at a point, all stress components for another set of orthogonal planes can be calculated.

Free energy in thermodynamics is expressed as Helmholtz energy $U - TS$ (U is the internal energy, T is the temperature, and S is the entropy) or as Gibbs energy $H - TS$ (H is the enthalpy). Because $H = U + PV$, the Helmholtz energy can be conveniently viewed as a special case of the Gibbs energy in which the pressure-volume effect is minimal. When a solid

material is stressed, its springlike response is typically a result of an increased internal energy U. This mechanical energy is predominantly associated with a change of shape, although a small contribution may come from the strain-induced volume change. There is another type of strain energy that is not attributable to a raised internal energy. Polymer scientists are familiar with such an exceptional case with rubbery polymers in which the deformation hardly affects the internal energy U, but results in the decrease of entropy S, thus raising the Helmholtz energy. In all these cases, the mechanical energy is viewed as a type of thermodynamic free energy. Similarly, the electrically raised energy in dielectrics is also a type of free energy. Dielectric relaxation means that a stored (capacitive) free energy is dissipated as heat (resistive). If the resistance were zero, the entire energy could be stored and returned, and we would have a perfect capacitor.

Finally, one important comment should be made on a practical aspect of the strain energy when it is subject to relaxation. When a material capable of relaxation is strained, the stress will decay even when the strain is held constant. The elastic free energy is being dissipated as the molecules transit from the initially raised energy level (strained state) to the final equilibrium state. With the pressure-volume model, this is comparable to allowing the compressed gas to leak through a small hole in the chamber wall; the density will decay back to the uncompressed equilibrium value in time. However, at each step during this decay process in which the free energy is decaying (i.e., NOT in equilibrium), the precise thermodynamic relationship between the pressure and the specific volume is maintained. Similarly, even though the final equilibrium value of the relaxing stress is 0, at each step during the decay of stress, the precise relationship according to the law of *elasticity* is maintained between the stress and the free energy. This free energy is a measure of how much capacity to do work remains in the material but *not* how much work has been done to the material. The measurable (laboratory) strain is a measure of work that has been done, and it is *not* the strain ε in Equation 1.1.3. Rather, ε in that equation is the *elastic* portion of the measurable strain, and the equation can be considered to be the implicit definition of this parameter.
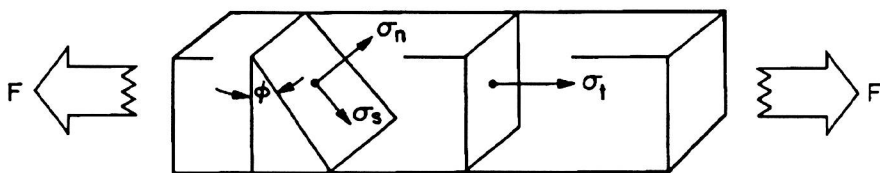
Figure 1.2.1 Force F on the rectangular bar induces the stress, the magnitude of which depends on the choice of the angle of cross section.

1.2 Interrelationships Among the Stresses in an Elastic Body[1]

We stated in the preceding section that the elastic (free) energy density Ψ at a point within the material is equal to the total sum of all stress components at the point. Since there are three orthogonal planes at each point and one normal stress and two shear stress components in each plane, nine stress components completely describe the state of stress at each point. The value of each stress component depends on the choice of the directions of the three orthogonal planes with respect to the external forces acting upon the body, but the elastic energy is constant as long as the external forces are constant. It is possible to consider several classes of elastic energy. For example, there is the energy that is related only to the hydrostatic stresses. The strain related to this kind of energy is compressive or expansive. The sum of three stresses, each normal to one of the three orthogonal planes, is independent of the angles and is called the *invariant.* By the same reasoning, the sum of all stresses that contribute toward changing the shape of the body is another type of invariant. Later we will use these invariants in stress analyses involving viscoelastic and viscoplastic behavior; here, we illustrate how the concept of invariants is used in simple elastic stress analyses. Consider a rectangular bar being pulled by forces F at both ends, as shown in Figure 1.2.1. For the plane perpendicular to the direction of F, the stress

1. Timoshenko, S., and Young, D. H., *Elements of Strength of Materials,* 5th ed., Van Nostrand Reinhold Co., New York, 1968

σ_t acting normal to this plane is the only component that is not 0. There are no shear stresses. Two other planes orthogonal to this plane have no stress components either. Thus for this choice of three planes, there is only one stress component and it is σ_t, which equals F/A.

Now, consider another plane which makes an angle ϕ with F. There are two components this time, the normal stress σ_n and the shear stress σ_s. The intensities of these stresses are:

$$\sigma_n = \frac{F}{A} \cos^2\phi \tag{1.2.1}$$

and

$$\sigma_s = \frac{F}{A} \sin\phi\cos\phi = \frac{1}{2}\frac{F}{A}\sin 2\phi \tag{1.2.2}$$

Thus, when ϕ is 45°, $\sigma_s = \sigma_n = (F/2A)$, and it is the maximum value for σ_s. The plane that makes an angle of -45° is orthogonal to the plane above. The stresses are a mirror image of those above, meaning the normal stresses are in the opposite directions and the shear stresses are in the same direction. The sum of all stress components, four in all, is again F/A, since the third orthogonal plane has no stresses. Thus, the sum of the stresses is always found to be equal to F/A. The choice of the coordinates does not alter the sum.

Here is another example. We will now consider a two-dimensional problem with a plate subjected to two forces, F_1 and F_2 that are perpendicular to each other as shown in Figure 1.2.2. For the plane that makes angle ϕ with F_1, the two stresses are

$$\sigma_{n1} = \frac{F_1}{A_1}\cos^2\phi + \frac{F_2}{A_2}\sin^2\phi \tag{1.2.3}$$

and

$$\sigma_{s1} = \frac{1}{2}\frac{F_1}{A_1}\sin 2\phi - \frac{1}{2}\frac{F_2}{A_2}\sin 2\phi \tag{1.2.4}$$

and for the plane orthogonal to the above plane, stresses are: