

## LITHOPLATE PHOTOPOLYMER WEAR MECHANISMS

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In recent years, I have been studying the solid-state properties of polymers and polymer composites and have been attempting to correlate these properties with the various mechanisms of abrasion and wear. The objectives were to delineate the specific properties of composites required for satisfactory performance as a support for the development of new or improved products and the development of satisfactory tests for quality control. In this framework, problems were examined that related to photopolymers that have been used in lithography.

This talk will be divided into three sections. The first section is background material, which defines and describes the nature of abrasion and wear and also describes the physical properties of the polymer compositions relevant to the study of wear. The second section describes a lithographic system in terms of abrasion and wear parameters. In the last section, examples are given of the kinds of information that are learned, with emphasis on their usefulness in the development of new and improved plates and how they can be a guide to the lithographic industry. The wear mechanisms and processes that will be described have also been observed and characterized for actual litho products. However, for this presentation, the study will be presented in reference to prototypes of lithoplate structures rather than to specific products.

### Wear and Wear Processes

Abrasion and wear is the systematic loss of material in the interface of two moving surfaces held in close contact. The rate of wear of surface material depends upon the molecular and bulk properties of the polymer,

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the surface topography, and the wear environment. The wear environment includes such factors as: (1) the force holding the surfaces in contact, (2) the condition of motion (rate and type such as impinging, rolling, sliding, periodic), (3) the temperature, and (4) the presence of interfacial material (e.g., lubricating films). The properties of the polymer and the roughness of the surface are characteristics of the product. The wear environment is dictated by the process and may or may not be changeable.

Wear processes are due to the frictional forces in the system. These forces, which are proportional to the applied force and the area of real contact\* for the two surfaces, can be separated into two components: a force of adhesion and a force of deformation. The first component arises from the formation and rupture of small adhesions in the areas of real contact. When surfaces are very clean and/or the forces holding the surfaces in contact are high, adhesion can form at the point of contact. The force is the work required to separate or rupture these adhesions as the surfaces separate.

The other component involves the deformation of the material. This deformation may be compressive, shear, or tensile. The deformation involves surface asperities that are flattened, folded, or stretched as the two surfaces move or asperities on one surface (or foreign material) indenting the second surface.

#### Physical Properties of Polymers

Materials respond differently to these forces. For example, mechanisms involving the formation of adhesive

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\*Area of real contact: All surfaces (even smooth surfaces) contain irregularities called asperities. On a macroscopic scale, the surfaces may appear smooth and in contact across the total area. However, on a microscopic scale, the surfaces are in contact only at the asperities.



Apparent Area  
Points of Real Contact

joints and subsequent rupture are characteristic of metal surfaces, whereas mechanisms involving deformation are more predominant in polymeric systems.

There are three mechanisms of abrasion and wear for polymers: adhesive, abrasive (microcutting) and cyclic deformation leading to failure. The physical characteristics associated with adhesive and abrasive wear mechanisms describe glassy polymers that are brittle and tend to fracture or tear easily when strains are low (Figure 1).

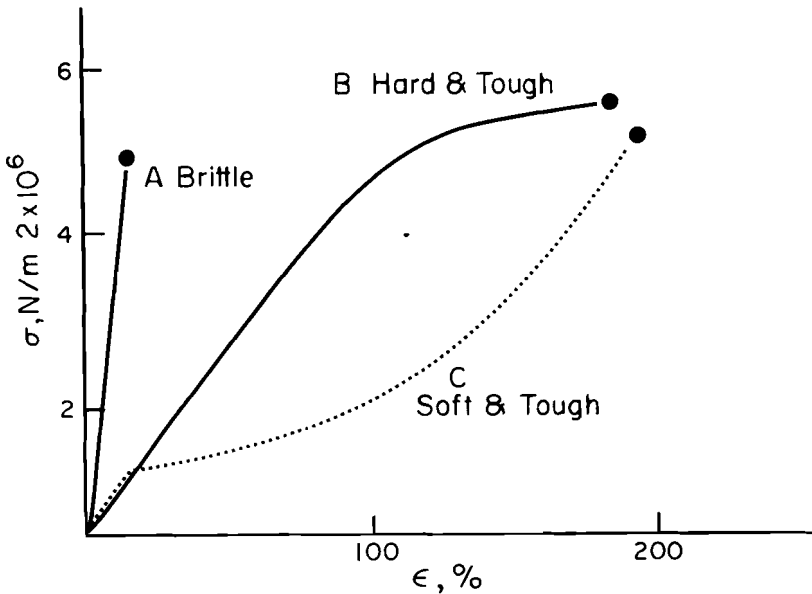


Figure 1. Viscoelastic behavior; stress  $\sigma$  vs. strain  $\epsilon$ .

The cohesive strength of the material in the abraded surface is usually less than the strength of an abrading particle or an interfacial bond formed in an adhesion. This adhesion will form as a result of surface interactions due to pressure and chemical affinity between components in the surface, and when the adhesion couples with a polymer with low strength, that polymer will fail cohesively and transfer.

Deformation and recovery are characteristic of materials that show viscoelastic behavior (rubberlike) (Figure 1). More simply expressed, these materials can be

deformed (stretched, twisted, flexed, compressed) at higher strain levels than brittle materials without rupture and will still return to their original shape. Most of the work done in deforming the material is recovered in each cycle; however, part of the work is dissipated as heat and is thus lost (Figure 2). When the deformations are periodic, this dissipation will lead to a slow deterioration of the polymer and to ultimate failure, which is termed fatigue.

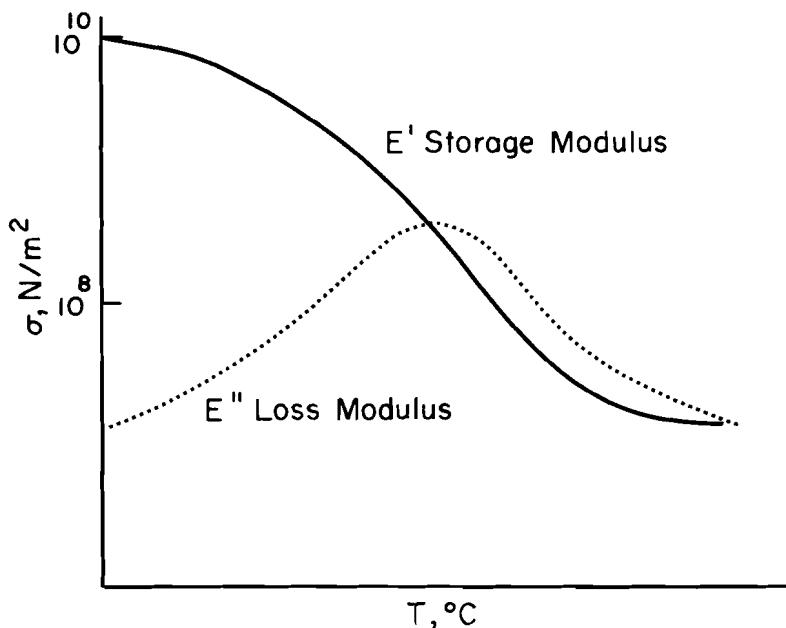


Figure 2. Dynamic mechanical spectra; storage modulus  $E'$  and loss modulus  $E''$  as functions of temperature.

The mechanical properties of polymers are dependent upon their molecular structure, molecular weight, cross-linking, the presence of other components or additives in the system such as plasticizers or reinforcing fillers, and temperature. At low temperatures, the polymer will behave as a "glassy material" (hard, inelastic, and perhaps brittle). At higher temperatures, its response will be viscoelastic (compliant, elastic). Between the two extremes, there is a temperature range where the transition

from glassy to viscoelastic behavior takes place (glass-transition temperature) (Figure 3). Plasticizers or

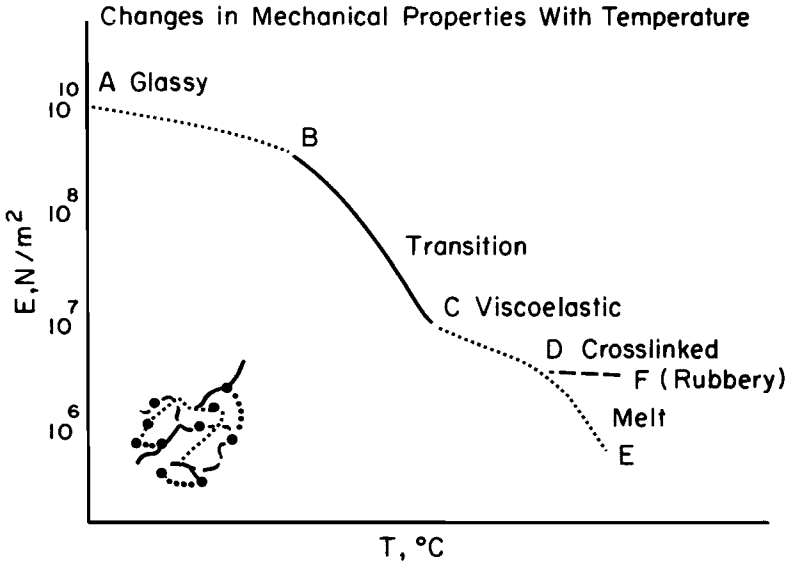


Figure 3. Changes in mechanical properties with temperature,  $E$  vs.  $T$ .

reinforcing fillers modify the mechanical properties by lowering or increasing the modulus. These changes may shift the onset of the transition from glassy to viscoelastic behavior to higher or lower temperatures (Figure 4).

#### Characterization of Wear

Wear can be identified by observing changes in the surfaces and by isolation and characterization of the debris formed. When the polymers are glasslike, the failure will tend to be brittle fracture. In adhesive wear, pits will be formed in one surface (A in Figure 5). Fragments of surface A will be found adhering to surface B after the surfaces separate. The dimensions of the debris and the pits are approximately the dimensions of the adhesions formed. The onset of this wear occurs when the surfaces make contact.

In abrasive wear (or microcutting), the surface will be scored with marks or furrows. The material will be

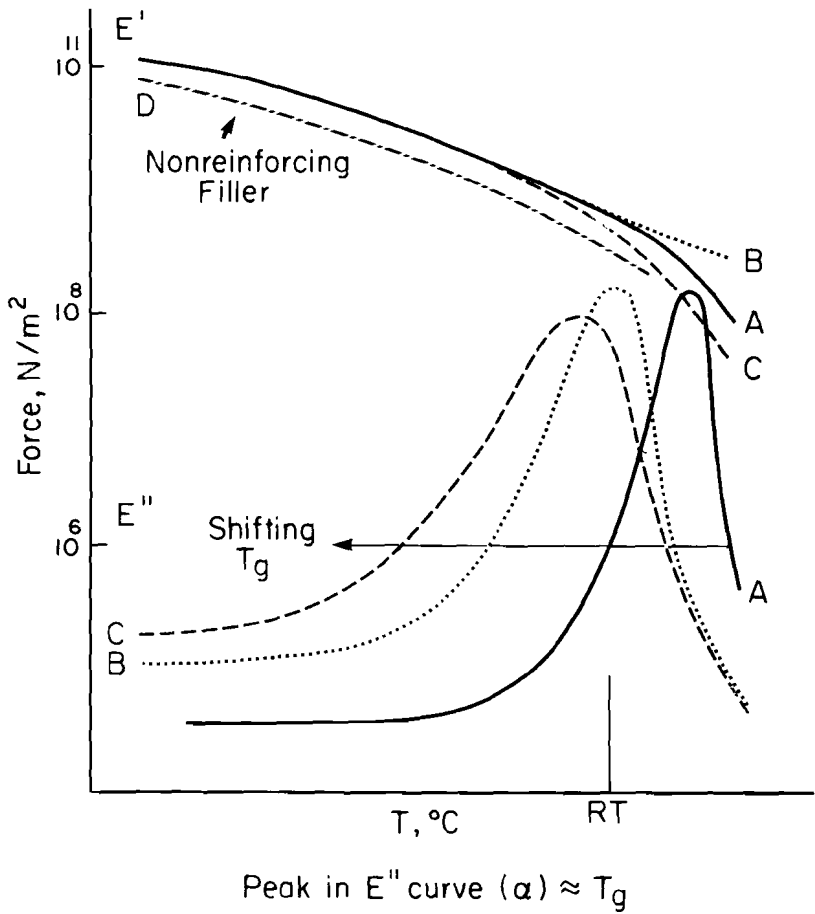


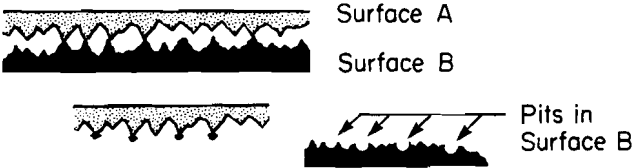
Figure 4. Dynamic mechanical properties showing changes in properties with nonreinforcing fillers or with plasticizers.

displaced to either side or to the end, or pits will occur where chips were cut out. The dimensions of the chips and the width of the furrows coincide with the dimensions of the abrading particle. The onset of this wear also occurs at the beginning of contact (Figure 5B).

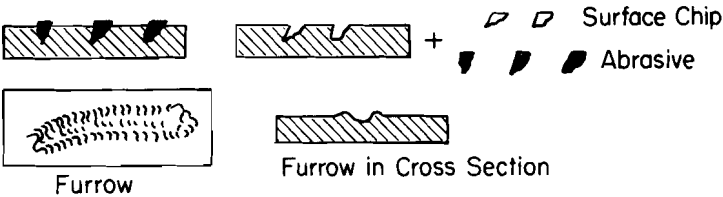
In fatigue wear, the surface will have cracks and fissures. Frequently, there will be evidence of delamination. The debris formed will be much larger than that

observed with the other two mechanisms. The onset of this type of wear depends upon the number of cycles of deformation and recovery required to cause fatigue (Figure 5C).

A) Adhesive Transfer



B) Abrasive



C) Fatigue

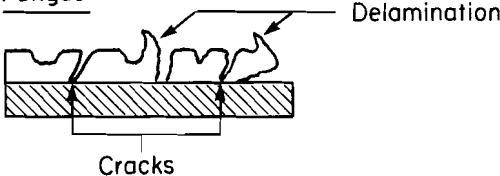


Figure 5. Surface changes and debris for wear mechanisms.

Description of a Lithographic System in Terms of Abrasion and Wear Parameters

Wear Environment

Offset lithography is a cyclic printing process in which there is sequential application of a wetting solution and an ink followed by transfer of the image first to a compliant roll (blanket) and then to paper. Figure 6 gives a schematic drawing of a lithographic press, showing the functional parts of this process: lithoplate mounted on a cylinder A, roll B for delivery of fountain solution, form rolls C for ink delivery, and blanket D. Arrows denote the sites and directions of various forces applied

to the plate during a press run. During one revolution, the plate is subjected to a number of stresses arising from the mechanical action of the rolls. At the form roll, there will be a compressive force at the nip of each roll ( $\sim 1$  pli), a tensile force as the ink separates from the form roll to the plate, a shearing force coupled with a tensile stress parallel to the plane of the plate and in the direction of rotation as the plate passes through the various nips, and a stress from the induced flow pattern caused by the vibrator roll. At the blanket, there will be a compressive force at the nip ( $\sim 80$  to  $150$  pli) and tensile stresses as the ink splits from the plate to the blanket. Because the lithographic process is cyclic, the stresses applied to the plate are periodic. Therefore, there is a high probability of fatigue wear.

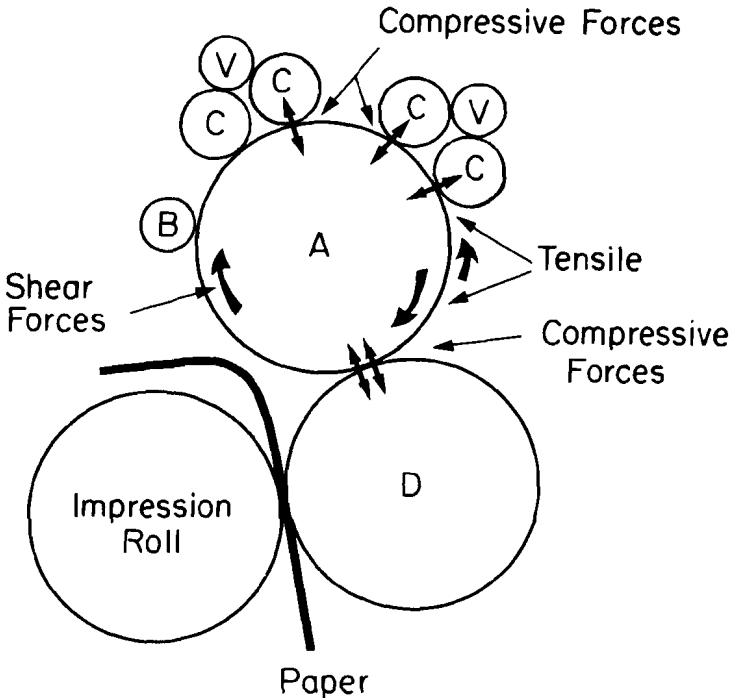


Figure 6. Schematic drawing showing functional parts of a lithographic press.

In this system, the ink is the interfacial material. Inks are viscous dispersions of pigment particles, which are not lubricating, but are abrasive. During the ink



application to the plate, abrasion is caused by the movement of the particles over the surface of the plate. The magnitude of abrasion will depend upon the forces applied in the nip, the distance over which the particle travels, the rake angles (cutting edge) of the particles, and the particle size.

### Polymer Properties

The photopolymers used on lithographic plates are rendered insoluble by a light-induced, chemical reaction to form a network called crosslinking. The initial molecular weight of the polymer before crosslinking and the crosslinking density can strongly influence whether a material is glassy or viscoelastic.

### Surface Structure

Surface structure (or roughness) is an important parameter in wear. However, its contribution to the types of wear, which would be expected, is also dependent upon the physical properties of the polymer. This dependence can best be described by using prototypes of lithoplate structures where increased roughness is introduced (Figure 7). The structures consider only a crosslinked,

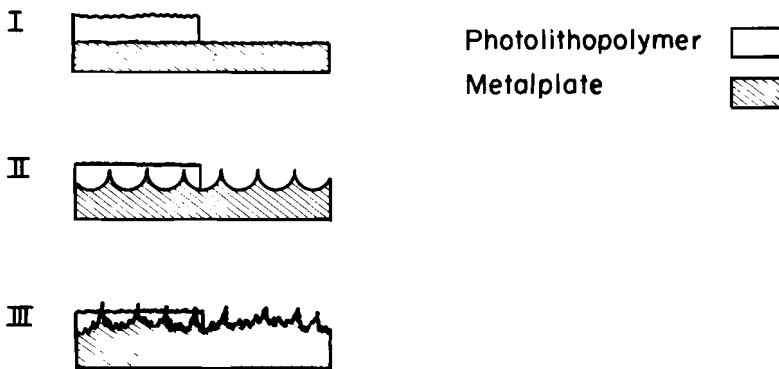


Figure 7. Prototypes of lithoplate structures.

photopolymer layer coated on a metal substrate. In the three prototypes, it is assumed: (1) that the adhesion of the photopolymer to the substrate is satisfactory, and that in the initial stages of wear, delamination does not

occur, (2) that the photopolymer forms the ink-receptive layer, and (3) that the metal surface of the support provides the litho surface. In prototype I, the support is a metal sheet, which is essentially flat, untextured, and shows a minimum degree of roughness. In prototype II, the metal support is mechanically abraded to introduce moderate roughness. In prototype III, the surface of the metal has been treated to make it very rough. The highest peaks of the asperities in the textured surface protrude through the photopolymer layer.

The coatings for these surfaces, which are prepared with glassy photopolymers, will microcut under the action of abrasive ink. In the first model, the predominant mechanism will be abrasion of the polymer. The rate of wear can be correlated with the force and the size and shape of the pigment in the ink. Fatigue and stress-induced delamination may occur late in the wear-life profile, but the contribution of this type of wear should be significantly less than that of abrasive wear (Figure 8, curve 1).

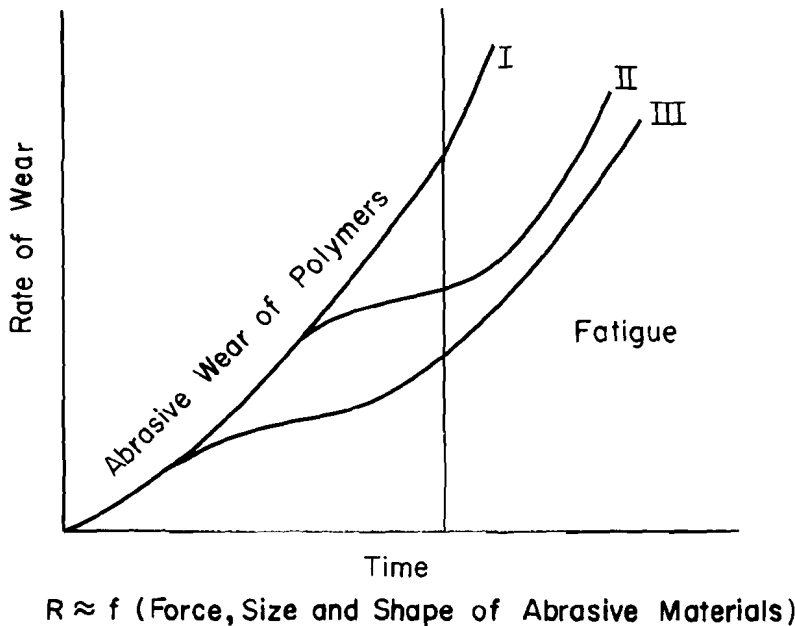


Figure 8. Wear profile of glassy polymers.

In the second model, the initial mechanism of wear would be that of abrasion. Once the metal asperities (or peaks) are exposed, the rate-controlling mechanism would be abrasion or polishing of the metal peaks. These peaks act as a spacer and reduce the effective force applied to the polymer for abrasive action. With time, the onset of fatigue occurs. The two types of wear make significant contributions to the total wear observed (Figure 8, curve 2).

In the third example, the initial wear occurs at the peaks. The bulk of the polymer layer is found in the valleys or interstices of the rough structure. Abrasive wear is minimized because the force applied directly to the polymer will be less. Under these conditions, the dominant mechanism of wear would be failure as the result of fatigue.

Whenever the photopolymers can respond and recover from deformations, the predominant wear mechanism will be fatigue. The rate of wear will depend upon the maximum stress or strain applied directly to the polymers. Higher stress or increased frequency will lead to earlier onset of fatigue. When the polymer is more exposed to the various periodic stresses (compression, shear, tensile, etc.) as in prototype I (Figure 9, curve 1), the potential stress level is higher and the magnitude of the deformations is greater. In prototype III, the periodic stresses should reduce to tensile and shear forces that occur when the ink splits from one surface to the second. By keeping these forces at a minimum, the wear life can be extended (Figure 9, curve 2).

When the forces applied to the polymer exceed a maximum stress characteristic for the material, the polymer will fail because of tearing, etc. Abrasive action by fillers (pigments in inks or fillers in the polymer) is reduced because the polymer deforms rather than fractures.

For polymers in their glass-transition range, the fraction of the work dissipated as heat is significantly higher. The materials, therefore, will be more sensitive to failures arising from degradation and fatigue. The predominant mechanism is dependent upon the temperature of the system relative to the glass-transition temperature of the material. Any change that shifts the onset of the

glass transition in these systems will change the predominant mechanism of wear. This system will be more sensitive to plasticizers or reinforcing additives.

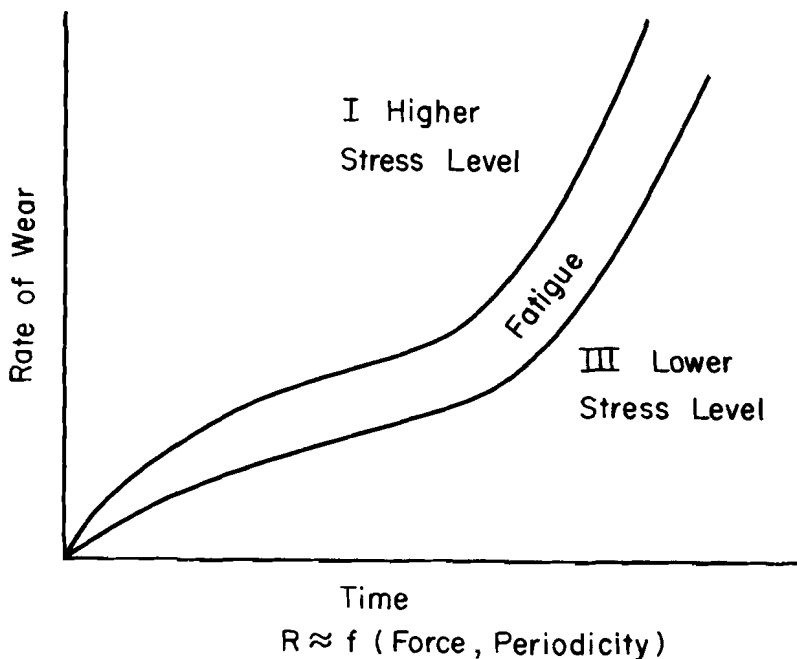


Figure 9. Wear profile of viscoelastic polymers.

With polymers there are contributions from both mechanisms of wear in that brittle fracture and fatigue are always present. Changes to minimize one type of wear will often increase the contribution from another type.

#### Applications

There are more than two components in a typical litho-plate. Several layers or addenda are added to enhance various features that the art of lithography dictates as desirable. Frequently, these additions result in interactions between the layers or components that will either increase or minimize wear. These interactions can be isolated in model systems, and their effect upon the mechanical properties can be systematically examined. The contributions of these interactions can be illustrated by examining examples of changes that affect the crosslinking

density. Crosslinking density may decrease as a result of (1) interference in exposure by added filler, (2) cage reactions associated with the sensitizer, (3) degradation reactions from overexposure, or (4) cavitation in composites filled with nonreinforcing filler. Mechanically, these changes would appear as a decrease in cohesive strength, as plasticization with a shift of the onset of the glass-transition temperature, and as a change in the viscoelastic response.

Interactions with solvents in the ink dispersions, wetting solutions, and the developers lead to swelling. Swelling in polymer compositions is dependent upon the extent of crosslinking and the solubility parameters of the solvent. In lithography, a controlled amount of swell is necessary in plate processing and also in the initial application of ink. However, excessive swell leads to plasticization and a shift of the onset of the glass transition to lower temperatures. This shift should lead to an increase in wear from fatigue, whenever the operating temperature of the press is in the range of the glass transition of the polymer. Excessive swell can be minimized by increasing the crosslink density, which decreases the elasticity (Figure 10).

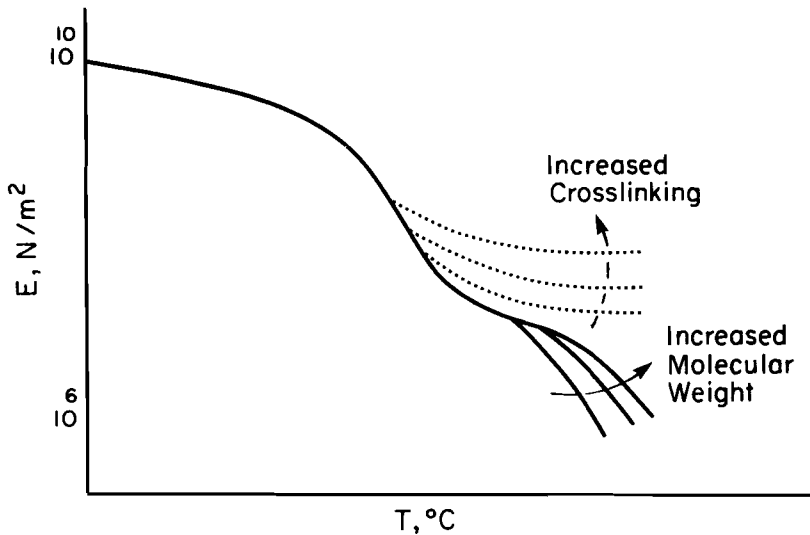


Figure 10. Change in mechanical properties with crosslinking and with increasing molecular weight.

If, however, the degree of swell is an essential characteristic of the system that cannot be minimized, an increase in the cohesive strength of the polymer without changing the crosslink density would lead to a decrease in the rate of fatigue wear. Cohesive strength can be modified by changing the molecular weight or the molecular weight distribution of the prepolymer or by adding reinforcing filler (Figure 10).

### Conclusion

In abrasion and wear of polymeric materials, there are several mechanisms that can be characterized by changes in the polymeric surfaces, by characterization of debris, and by characterization of wear profiles. Various mechanisms are associated with specific solid-state properties of polymers. The interactions in litho systems, which affect the mechanical properties of a polymer, can be studied in model systems. Knowledge of the polymer wear mechanisms and the contributions of interactions with other components in the system provides options for introducing new concepts or for improving products.

For the lithographer, this information should lead to a better understanding of all adjustments required in the art of lithography. He controls the wear environment for the lithoplate. He can manipulate the forces applied to the plate, he can select the interfacial material, or he can introduce a plasticizer.