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by Robert L. Fusaro
Lewis Research Center
Cleveland, Ohio 44135

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by Robert L. Fusaro

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

The friction characteristics of polyimide films bonded to metallic substrates were studied from 25° to 500° C. These results were interpreted in terms of molecular orientation and thermomechanical data obtained by torsional braid analysis (TBA). A large friction transition was found to occur at 40°±10° C in a dry argon atmosphere (10 ppm H_2O). It was postulated that the mechanical stresses of sliding transform or reorder the molecules on the surface into a configuration conducive to easy shear, such as an extended chain. The molecular relaxation which occurs in this temperature region appears to give the molecules the necessary freedom for this reordering process to occur. The effects of velocity, reversibility, and thermal prehistory on the friction properties of polyimide were also studied.

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INTRODUCTION

Technology today is placing ever increasing demands on polymers. Polymers are needed which have improved mechanical properties as well as having thermal stability at higher temperatures. One new class of thermally stable organic polymers which has demonstrated increased capabilities in these areas is polyimide. Polyimide refers to a general class of long chain polymers which have recurring imide groups as an integral part of the main polymer chain. By varying the monomeric starting materials and by controlling thermal prehistory, it is possible to tailor the polymer's mechanical properties while still maintaining the basic polyimide structure (1-4).

In the field of lubrication, polyimide usage is continually increasing. Solid bodies of polyimide, with or without solid lubricant additives, are being considered for bearings and seals, and in prosthetic human joints (5-7). In addition, polyimides have been used to bind solid lubricants to metal surfaces. Pyrolin polyimide (PI-4701) has been shown to be a good binder for the solid lubricant graphite fluoride $(CF_{1.1})_n$ (8-9) and for molybdenum disulfide (10).

The lubricating properties of polyimide films with no solid lubricant additives were studied in references 9 and 11. These studies revealed that a transition in the friction and wear life properties of these polyimide films existed somewhere between the temperatures of 25° and 100° C. At temperatures above this transition, the films exhibited much longer wear lives and considerably lower friction coefficients.

This investigation was conducted to determine the friction transition temperature more precisely and to investigate mechanisms that might be responsible for these transitions. The latter was attempted by comparing the friction properties of polyimide to molecular relaxations that are thermally induced in polyimide and by considering different molecular models of polymer structure. The molecular relaxation data were obtained by a dynamic mechanical technique called torsional braid analysis (TBA) (2-4). These tests were conducted for NASA at Princeton University by DR. J. K. Gillham.

BACKGROUND

Molecular Relaxations in Polymers

It is well known that most polymers have a glass-transition temperature T_G which marks their change from a rubbery to a glassy state. It is not so well known that most polymers also have secondary transitions below their T_G (12-24). Some of these secondary transitions appear to influence the mechanical properties of polymers (18). Where and why these transitions occur has thus become the subject of continuing research (1-4, 12-24).

Both the glass transition and the secondary transitions can be related to one or more molecular relaxation processes (changes of motion within polymers chains). The glass transition has been related to the motion of longer segments of the main chain; while the secondary transitions have been related to rotations or oscillations of side chains, subgroups, chain ends or shorts segments of the main chain (16-19).

There are several methods now in use for studying the molecular relaxation phenomena. Among them are nuclear magnetic resonance (rf energy absorption), dielectric energy absorption, and mechanical energy absorption. Essentially, all three methods consist of applying a force to the polymer molecules and then observing the energy absorption peaks that take place at various temperatures. By comparing the position and the size of the peaks, it is possible to deduce what type of molecular motion has taken place.

Molecular relaxations tend to be frequency dependent as well as temperature dependent (16,18), that is, the absorption peaks tend to move to higher temperatures as the applied frequency is increased. For this reason, in this investigation, correlation has been made between friction data (taken at relatively low frequencies) and mechanical energy absorption data also taken at low frequencies (~1 Hz).

Torsional Braid Analysis

The technique used to obtain the mechanical absorption spectra of polyimide was torsional braid analysis (TBA). The method is described in detail in references 2,3,4, and 12. A schematic drawing of the apparatus is shown in figure 1 (from ref. 4). The method uses an oscillating torsional pendulum, which consists of a glass braid impregnated with the polymer to be evaluated. Two quantities can be determined by evaluating the mechanical oscillations of the pendulum: the elastic part of the complex shear modulus G', and a quantity called the logarithmic decrement δ, which is a measure of the ratio of the energy dissipated to the maximum energy stored during mechanical deformation. Because of the nature of the specimens used, an absolute value of the elastic modulus G' is difficult to calculate. Since $G' = K(1/p)^2$, a measure of G' can be expressed in terms of $1/p^2$, where K is a constant for a particular specimen and p is the period of oscillation. This quantity $1/p^2$ is thus defined as the relative rigidity of the polymer (2-4, 12).

Models of Polymer Structure

Polymers may be classified as being either amorphous or crystalline; however, even in well-crystallized polymers, amorphous regions have been found to exist (25-29). Likewise in amorphous polymers, crystalline regions have been observed (25-29). Undoubtedly, the interaction of these regions, as well as the transformation from one phase to another, can influence the physical properties of a polymer.

In order to explain the various physical properties possessed by polymers, several models of polymer structure have been proposed. Some of the most prominent models are the following:

(1) Random coil (29-31)
(2) Fringed-micelle (25-27,30,32-36)
(3) Folded chain (19, 25-27, 36-39)
(4) Extended chain (40-42)
(5) Molecular domain (43)

Polyimide is a crystalline polymer (44). The model that is most widely accepted for crystalline polymers is the folded chain, it is based on the fact that complex aggregates of molecules, called spherulites, exist throughout the entire mass of solid polymers (25-28, 35, 36). X-ray diffraction studies have shown these spherulities to be composed of plate-like lamellae (19, 25-27). Although the thickness of these lamellae may vary, the lamellae formed for particular crystallization conditions are characterized by a rather uniform thickness of the order of 5 to 100 nanometers (50 to 1000 Å). Electron microscopy has shown that the lamellae consist of regularly folded chains which are perpendicular to the lamellae surface; thus, this model has been designated the folded-chain model.

Figure 2 gives a schematic representation of a polymer which has been crystallized under different conditions and has attained different degrees of order (10). Folded chains, extended chains, and the amorphous nature of the polymer can be seen. If the distance between the folds in the folded-chain model becomes greater than 200 nanometers, the crystal is designated as an extended-chain crystal (40, 41). When no folds are present, the term fully extended-chain crystal is applied.

There are several ways that extended-chain crystals can form. They can be formed from the melt by regulated crystallization conditions, they can be formed in a polymer solid by annealing it at temperatures above the crystalization temperature, or they can be formed by applying a mechanical stress to a polymer so as to induce chain unfolding (40, 41).

Two models for chain unfolding by the mechanical deformation of lamellae have been proposed (25, 42). The first proposes that by plastic deformation, the chains simply unfold in the direction of the applied force. The second proposes that, by shearing deformation, the chains gradually become tilted by twisting and slipping and thus become progressively oriented in the direction of the force.

EXPERIMENTAL PROCEDURE

Friction Apparatus

A hemisphere-on-flat sliding friction apparatus was used to study the polyimide friction transition. The friction specimens (fig. 3) consisted of a flat (6.3 cm diam) disk in sliding contact with a stationary (0.476 cm rad) hemispherically tipped rider. The wear track diameter on the disk was varied by changing the position of the rider. Thus, several tests could be performed on each disk on diameters that ranged from 3.8 to

5.8 centimeters. The apparatus was equipped with a variable-speed motor and gear reduction system so that the rotational speed could be varied from 10 to 1000 rpm.

Induction heating was used to heat the disk. A strain gage sensed the frictional force, which was continuously recorded on a strip-chart recorder or plotted as a function of temperature on an x-y recorder.

Surface Preparation and Cleaning

The hardness range of the 440C stainless-steel specimens used in this investigation was Rockwell C-58 to C-60. The disk surfaces were roughened by sandblasting to an rms of 0.9×10^{-6} to 1.3×10^{-6} meter. After sandblasting, the disks were cleaned by the following procedure:

(1) The surface was scrubbed under running water with a brush to remove abrasive particles.

(2) Then the surface was cleaned with pure ethyl alcohol.

(3) The surface was then scrubbed with a water paste of levigated alumina and cleaned until water wet the surface readily.

(4) Next it was rinsed under running water while brushing to remove the levigated alumina.

(5) Then it was rinsed in distilled water.

(6) Finally the surface was dried with dry compressed air. (Sandblasted surfaces not dried quickly had a tendency to oxidize.)

The riders were cleaned by the same procedure, but since they were not sandblasted, step 1 was not necessary.

Film Application

A thinner consisting of N-methyl-pyrrolidone and xylene was added to the polyimide varnish to obtain a sprayable solution. The polyimide solution was sprayed onto each disk by using an artists airbrush. The film did not dry rapidly. Thus, in order to eliminate "running", only a thin film of polyimide was applied at one time. The disk was heated at 100° C for 1 hour and then another thin film was applied, etc. When the desired thickness of 25±2 micrometers was obtained, the film was cured. The curing procedure was to heat the film at 100° C for 1 hour and then to heat it for an additional hour at 300° C.

Experimental Technique

The procedure for conducting the friction transition tests was as follows: A rider and a polyimide coated disk (polyimide was not applied to the rider) were inserted into the friction apparatus. The test chamber was sealed, and the desired atmosphere was purged through the chamber for 15 minutes before the test was started. The flow rate was 1500 cubic centimeters per minute. This flow rate maintained a slight positive pressure in the chamber whose volume was 2000 cubic centimeters. After the purge was completed, the disk was heated to the desired temperature. Then the disk was set into rotation, and the load applied.

In order to determine the temperature at which the large friction transition occurred, the temperature of the disk was raised to a temperature between 105 and 300° C and held constant for 15 minutes. The film was then "run-in" (process by which the friction coefficient goes from a high to a low value) at this temperature until a stable friction coefficient was obtained. The temperature was then gradually lowered until the friction transition occurred. Test conditions were a dry argon atmosphere

(10 ppm H_2O), a sliding velocity of 1.6 m/sec (600 rpm), and loads of either 500 or 1000 grams.

In order to determine the effect of velocity on the friction transition, a series of experiments were conducted in a dry argon atmosphere (100 ppm H_2O) with an applied load of 500 grams and at velocities of 0.027, 0.13, 0.27, 0.53, and 1.33 m/sec (10, 50, 100, 200, and 500 rpm). The test procedure for these experiments was to "run-in" the film at 150° C at 0.27 m/sec (100 rpm) for 5 minutes. The specimens were disengaged, and the desired test velocity was obtained. The specimens were reloaded and the friction transition was obtained as described in the previous paragraph. The specimens were then unloaded and the temperature of the film was raised to 150° C. The velocity was returned to 0.27 and the film was "run-in" for 5 minutes. The previous procedure was then repeated for a new test velocity. Several experiments were performed on the same wear track; the velocity was changed for each test in a random order.

In order to determine the correlation with TBA data, the polyimide film was "run-in" at 150° C in a dry argon atmosphere (10 ppm H_2O) until the friction stablized at a constant value. A load of 500 grams and a velocity of 1.6 meters per second were used. The temperature was first lowered until the friction transition occurred; then the load was removed, and the film heated to 150° C. The load then was reapplied and the film "run-in" again as previously stated. Next, the temperature was raised to 500° C at the rate of approximately 3° C per minute.

Temperature Measurement

Two methods of measuring temperature were employed. The first was an infrared optical pyrometer which could measure temperatures to as low as 30° C (estimated accuracy, ±2° C). By using this instrument, friction as a function of temperature was plotted directly on an x-y recorder. The second method was to use liquid crystals. Liquid crystals have the property of changing colors as a function of temperature. The liquid crystals were applied with a brush on the outer portion of the disk (outside the wear track). Extreme care was taken so that liquid crystal material would not get into the contact area. By visually observing the color change of the liquid crystals, the temperature of the disk could be determined (estimated accuracy, ±1° C).

RESULTS

Effect of Temperature

In a previous study (9, 11), it was noted that a large decrease in friction and a corresponding increase in wear life occurred for polyimide films somewhere between 25° and 100° C. One of the objects of this study was therefore to more precisely locate the temperature at which these phenomena occurred. Thus, a series of experiments were conducted in a dry argon atmosphere (10 ppm H_2O) at a velocity of 1.6 m/sec (600 rpm) and under a load of 1 kg (for details, see the section Experimental Technique).

A plot of temperature and friction coefficient as a function of time for a representative experiment is given in figure 4. For the first 10 minutes of the test the temperature was held constant at 105° C. The friction coefficient during this time went from a high value of 0.23 to a minimum value of 0.03. It took about 7 minutes of sliding time for this to occur. This process, which is referred to as "run-in", is believed to be an orientation phenomenon which only occurs at temperatures above the transition temperature. This was noted previously in reference 11, where it was found that, in dry atmospheres (10 to 20 ppm H_2O), a "run-in" process occurs at 100° C but not at 25° C. At 25° C, the friction coefficient starts at 0.20 or higher and increases in value with time until the film is completely worn away.

After 10 minutes of sliding at 105° C, the induction heating unit was turned off and the film was allowed to cool, as the temperature against time curve (fig. 4) illustrates. As the temperature decreased, the friction coefficient remained nearly constant at the value of 0.03. When the temperature reached 50° C, the friction coefficient suddenly increased. Upon further reduction in temperature, it reached a value of 0.25; a value equivalent to the friction coefficient obtained before "run-in". The induction heating unit was then turned back on and the temperature of the film slowly increased. Figure 4 shows that upon heating the transition is reversible; however, the friction coefficient did not return to its originally minimum value of 0.03 until the temperature was 64° C. This might be expected, since an orientation process is time dependent.

Figure 5 presents data points from five different tests which were performed under the same conditions as the data of figure 4, except that the temperature in these tests was decreased from 150°±10° C rather than from 105° C. The figure shows there is considerable scatter in the friction data below 90° C. Many other experiments were conducted on the location of the friction transition. The transition was determined by increasing the temperature from 25° C and by decreasing the temperature from various other temperatures (e.g., 300°, 240°, and 200° C, etc.).

Essentially, the temperature at which the large friction transition occurred was not greatly affected by these variations. The friction transition was not found to occur at one particular temperature; however, instead it was found to occur in the temperature region of 40°±10° C. The transition was found to be reversible in all instances, that is, it was independent of whether the temperature was increased or decreased through the transition region. A limitation of this reversibility was that a wear transition accompanies the friction transition. At temperatures below the transition, the wear rate of the film is much greater than at temperatures immediately above the transition. Since only thin films were applied (25±2 micrometers), the film quickly wore away if sliding continued for too long a time at temperatures below the transition. This wear phenomenon is currently being studied in more detail.

Effect of Sliding Velocity

In order to determine if sliding velocity had an effect on the friction transition, a series of experiments were conducted in a dry argon atmosphere (100 ppm H_2O), under an applied load of 500 gm, and at sliding velocities of 0.027, 0.13, 0.27, 0.53 and 1.33 m/sec. Three tests were performed at each velocity.

Table I presents data taken for each of these tests, as well as averages for each velocity. Given in the table are the temperature at which the friction coefficient first started to increase in value; the temperatures at which the friction coefficient reached values of 0.05, 0.10, and 0.20; and the number of sliding revolutions that elapsed before the friction coefficient reached values of 0.10 and 0.20.

The data from the table indicate that sliding velocity (in the range of 0.027 to 1.33 m/sec) was not a major factor in determining the temperature at which the friction transition occurred. The temperature at which the friction coefficient first started to increase (all tests included) ranged from 100° to 116° C; however, there is not any trend concerning velocity dependence apparent from these data. The same is true for the temperatures at which the friction coefficient reached values of 0.05, 0.10, and 0.20.

In figure 6 representative friction traces are plotted as a function of temperature. For the slowest test velocity (0.027 m/sec), the friction trace is rough and the value of the friction coefficient increased gradually with decreasing temperature. As test velocity was increased, the traces tended to become smoother (probably due to recorder response), and the friction coefficient tended to stay at a lower temperature. When the friction coefficient did increase, at higher test velocities, it seemed to do so at a faster rate.

Comparison to Thermomechanical Behavior

In a discussion included in reference 9, Solomon and DeGee compare the friction and wear life data of that paper to thermomechanical absorption data obtained by Gillham using the TBA technique (12). The data they use for comparison were obtained by Gillham on the polymer polybenzimidazole, not polyimide. Their main point is to suggest that there may be a correlation between the friction and wear life properties of polyimide and its own thermomechanical spectra. Thus, another of the objectives of this study was to compare the friction characteristics of the polyimide polymer P1-4701 to its own thermomechanical spectra, in an attempt to postulate why a large friction transition occurs for this polymer.

Figure 7 gives thermomechanical data (relative rigidity and logarithmic decrement) for the polyimide used in this study as obtained by TBA.[1] The experimental technique for obtaining the TBA data is summarized in table II. The peaks in the logarithmic decrement curve (fig. 7b) reveal loss maxima, that is, the temperatures at which maximum energy is absorbed. The loss maximum that occurs at the highest temperature is designated α, the next lower one β, etc. Table III summarizes the TBA results which were obtained for this polyimide.

It is seen in the data of Table III and the data of figure 7b that the position of α is dependent on the thermal prehistory of the polyimide. As the temperature was increased to 500° C, α appeared in the logarithmic decrement curve at 354° C. However, when the temperature was reduced from 500° C, no α-loss maximum appeared at 354° C. A similar result is found in the rigidity curve of figure 7(a); as the temperature was increased to 500° C, there was a sharp drop in the relative rigidity of the polyimide, which reached a minimum at 377° C. Upon reduction of the temperature from 500° C, no minimum occurred.

The lower temperature loss maxima, β and γ, were not noticeably affected by the thermal prehistory of the polyimide. β occurred at 179° C and γ occurred between -112° C and -113° C. The loss maximum designated β_{H_2O} was due to water. The dry nitrogen atmosphere contained very small quantities of H_2O, which upon cooling below freezing it cumulatively

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[1] Tests were conducted for NASA at Princeton University by Dr. J. K. Gillham

condensed on the walls of the chamber. The size of the peak points out how sensitive polyimide is to the adsorption of water, since the amount of water was very small.

The comparison of TBA data to friction coefficient data for polyimide films is shown in figure 8. Plotted on the figure are the logarithmic decrement and the friction coefficient as a function of temperature for a polyimide film cured in air at 300° C and for the same polyimide film after it was heated in argon to 500° C. The β_{H_2O}-peak has not been shown in this comparison since it only appeared (in a dry atmosphere) after the temperature was reduced to -190° C. When H_2O is present in the atmosphere, it is felt that this peak may have correlation to the friction properties of polyimide, but this is subject to future study. The friction traces shown were obtained by either increasing or decreasing the temperature at the rate of approximately 3° C per minute after the films had been "run-in" at 150° C (see section Experimental Technique). The friction trace shown in figure 8(a) was obtained on a polyimide film after it had been cured in air at 300° C. The friction trace shown in figure 8(b) was obtained on a slightly different wear track on the same film after it had been heated to 500° C in an argon atmosphere.

The thermal prehistory of the polyimide film did not seem to markedly affect the temperature at which the large friction transition occurred. In both cases there was a gradual increase in friction starting at about 110° C and then a large increase at about 40° C. For the film heated in dry argon to 500° C, a minimum value of the friction coefficient was obtained at about 180° C. This value corresponds to the β-loss maximum (which occurred at 179° C); but the change in friction is so slight, this minimum may only be an anomaly.

There appears to be no direct correlation between a loss maxima in the logarithmic decrement curve and the large friction transition (fig. 8(b). The loss maximum closest to the friction transition is β. It occurred at 179° C. The friction transition occurred at a considerably lower temperature, although there was a problem in defining an exact friction transition temperature. In most instances, the friction coefficient started to increase in value at about 110° C and then at about 40° C there was a large increase. Since the value of the friction coefficient at room temperature (25° C) was 0.20 or greater, the friction transition temperature was taken to be the temperature when the friction reached this value.

A closer examination of what the logarithmic decrement absorption peaks represent is necessary in order to make a correlation. The loss maxima represent the temperatures at which specific molecular motions achieve their greatest degree of freedom. Increasing the temperature above this point cannot produce further motion, but the specific motion involved continues unhindered. As the temperature is decreased below the loss maximum, the motion responsible for the loss mechanism is continuously hindered, until at some temperature it becomes completely frozen. This is the onset temperature of the absorption peak.

It seems reasonable to postulate that this onset temperature may be the temperature to which the friction transition temperature should be compared. In order to determine if there were any correlation, the first derivative of the logarithmic curve was taken. Unfortunately, in the temperature range where the large friction transition occurred, no distinct maximum in the derivative curve was found. The β absorption peak is of such a nature that there were no sharp inflections in the friction transition temperature region. However, a broad peak in the derivative curve was found in this temperature region, which indicated some molecular motion was taking place. Thus it is postulated that the friction transition may be related to the <u>onset</u> of the β absorption peak, and not necessarily to the <u>maximum</u> of the peak.

In the same regard, the change in the friction properties of the polyimide film above 300° C may be related to the onset temperature of the α-relaxation process. However, in this instance the molecular movement involved is detrimental to friction. This will be discussed in more detail in the next section.

Another effect found was the existence of a friction peak between 250° and 300° C. This peak was found to occur at 250° C for the 300° C cured film and at 300° C for the same film heated to 500° C. The reason for the peak is obscure; it may only be an anomaly.

DISCUSSION OF RESULTS

As discussed earlier, the mechanical properties of polymers are dependent on such factors as their molecular structure and the degree of mobility of their molecular chains. In order to determine if the large friction transition in polyimide films was related to molecular chain mobility, the friction data were compared to dynamic thermomechanical data obtained by the TBA technique.

A direct correlation between a loss maxima in the logarithmic decrement curve and the large friction transition temperature (fig. 8) was not found. The loss maximum closest to the friction transition was β, which occurred at 179° C. The large friction transition occurred at a considerably lower temperature.

A better correlation to a TBA loss maximum might be obtained if friction heating at the interface were taken into account. However, in terms of thermal energy supplied to the film, frictional heating is probably not significant. The contact area on the rider may get quite hot; but since the time duration of the rider sliding on any particular area of the film was so short, it is felt that the thermal energy supplied to the film was minimal. This is indicated by the fact that a pyrometer focused on the film wear track showed no discernible temperature rise from frictional heating and that varying the sliding velocity did not have a discernible effect on the friction transition temperature.

If correlation does exist, it most likely is related to the onset temperature of the relaxation peak. This is the temperature at which the molecular motion responsible for the loss mechanism is released from its "frozen state". As temperature is increased above the onset temperature, the motion increases until it achieves its maximum at the relaxation peak maximum (loss maximum). Considering this, a possible explanation for the friction transition might be that a certain degree of freedom (for some particular molecular segment) is necessary before the mechanical stresses of sliding can reorder the molecules into a configuration that is conducive to easy shear and thus low friction. As more is learned about polymer friction, it is becoming increasingly apparent that a certain degree of order must exist at the sliding interface if low friction is to occur. For example, Pooly and Tabor (45) have shown that when low friction occurred in the polymer PTFE, the molecular chains of this material were oriented in the sliding direction. Other researchers have also observed similar molecular order with PTFE and other polymers (46-51).

The results of this study suggest that polyimide also undergoes an ordering process. However, unlike PTFE, a certain thermal energy must be supplied to the polyimide molecules to enable the mechanical stresses of sliding to reorient them into a structure conducive to low friction. It is possible that the friction properties of PTFE may also be related to molecular relaxations (52). At temperatures below ambient, PTFE exhibits high friction; and there is a relaxation peak in this temperature range for PTFE which may correlate to this change in friction characteristic.

Considering the structure of polymers (see section Background), a possible explanation for the friction transition might be the transformation of folded chains into extended chains. As a result of shearing deformation, the chains become progressively oriented in the direction of the stress. The fact that the friction transition is reversible indicates that the molecules may revert to their original structure if insufficient thermal energy is supplied.

Optical microscopic observation of the polyimide film wear tracks indicated that a wear transition accompanies the large friction transition at 40°±10° C; and that if orientation takes place, it is limited to the very near surface. These phenomena are currently being studied in more detail.

Gillham (2-4) believes that heating certain polyimide films to 500° C has the effect of shifting the α-loss maximum to a temperature greater than 500° C. This is supported by the rigidity curve of figure 7(a). As the temperature was increased to 500° C, there was a sharp drop in the relative rigidity of the polyimide, which reached its minimum at 377° C. Upon reduction of temperature from 500° C, no minimum was found. It is also supported by optical microscopy studies of the polyimide film wear tracks, after they had been run to 500° C in the friction tests of this study. Observation of the wear track on a polyimide film (cured at 300° C), after it had been tested to 500° C, showed that the central portion of the wear track had been worn away exposing the metal substrate. Observation of a wear track on a polyimide film, which had been previously heated to 500° C in argon and then tested to 500° C, showed that the film was still intact on the wear track. This indicates that heating the film to 500° C before testing gave it greater strength.

It is postulated that there may be some correlation between the change in the friction properties above 300° C and the onset of the α-relaxation peak in the TBA curve. A possible reason for the increase in friction above 300° C, may have been due to the fact that the rigidity of the polyimide film was decreasing and could not support the rider load; thus the film was worn away until the rider was partially supported by the metal substrate and the polyimide film (see fig. 9). The erratic nature of the friction would then be due to the type of contact involved, part metallic and part polyimide. When the film was heated to 500° C, the rigidity was increased at temperatures above 300° C and the film was able to support the load.

The α-loss maximum is usually considered to denote the glass transition temperature T_G; that is, it is the temperature where the material changes from a rubbery to a glassy state or the reverse. On a molecular level, it is considered to denote the temperature at which large-scale movements of the molecular chain can take place (18). By heating the polyimide to higher temperatures, a more complete polymerization (post polymerization) may take place, such as chain extension, crosslinks, etc. This would inhibit large-scale molecular movements, thus making the polyimide much more rigid at the higher temperatures. It should be noted that the curing temperature cannot be increased substantially in an air atmosphere, since polyimide oxidizes at elevated temperatures.

No mention thus far has been made of the γ-peak or the β_{H_2O}-peak. Since both of these peaks occur below the friction transition temperature, the molecular motions associated with them extend through the region of the friction transition. Thus, it could be that the motion associated with the γ-peak is a factor contributing to the friction transition. The friction results from references 9 and 11 indicated that when H_2O was present in the test atmosphere, detrimental friction and wear life results would be obtained. Thus, the molecular relaxation associated with the β_{H_2O}-peak may be detrimental to producing an ordered film at the interface.

In summary, it has been postulated that there may be some correlation between the onset of the β-relaxation peak in the TBA logarithmic decrement curve and the large decrease in friction that occurs at about 40°±10° C. It has been suggested that the mechanical stresses of sliding coupled with a new mode of molecular motion may induce changes in the molecular orientation at the surface of the polyimide film wear track. While these postulations are not proven conclusively by the results, they offer a plausible explanation for the friction transition. More conclusive experiments should be conducted to verify these postulates, and to try to pinpoint what particular molecular movement is responsible for the transition. Unfortunately, the molecular structure of this particular polyimide was proprietary, but preliminary experiments indicate that this friction transition phenomenon occurs in other polyimides. Thus it is planned to correlate the friction properties of polyimides, which have known molecular structures, to their own particular TBA spectra. In this way a more definitive correlation can be achieved.

SUMMARY OF RESULTS

Correlation of experimental friction results and torsional braid analysis (TBA) results on a polyimide film, along with a literature study of polymer structure, have yielded the following results:

1. When the temperature was lowered from elevated temperatures (140° to 300° C), at the rate of approximately 3° C per minute, a gradual increase in friction was found to commence at about 110° C and a large increase occurred at 40°±10° C.

2. The friction transition was found to be reversible in all instances, that is it was independent of whether temperature was increased or decreased through the transition region. It was also found to be independent of sliding velocity (in the range of 0.027 to 1.33 m/sec).

3. No direct correlation was found between the friction transition and the loss maximum of any relaxation peak in the TBA logarithmic decrement curve; however it is postulated that their may be correlation between the

onset temperature of a relaxation peak and the friction transition.

4. It is postulated that a new mode of molecular motion is initiated in the temperature region where the friction transition occurs. This new motion coupled with the mechanical stresses of sliding reorder the molecules into a configuration (at the surface only) which is conducive to easy shear. Such a configuration might be an extended chain.

5. Heating the polyimide film in argon to 500° C, increased the relative rigidity of polyimide at temperatures above 300° C and gave improved friction properties above 300° C.

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TABLE 1. - EFFECT OF VELOCITY ON THE FRICTION PROPERTIES OF POLYIMIDE FILMS

[Load, 500 g; riders, 440C stainless steel; atmosphere, dry argon (100 ppm H_2O).]

Wear track / Order of testing	Rotational speed, rpm	Sliding (linear) velocity, m/sec	Temperature (°C) at which friction coefficient-				Number of revolutions (cycles) before friction coefficient reached values of-	
			Started to increase	Reached values of-				
				0.05	0.10	0.20	0.10	0.20
1-5	10	0.027	108	92	72	54	166	273
2-3			102	62	53	47	275	328
2-5			103	68	48	44	319	380
Average			104	74	58	48	253	327
1-2	50	0.13	108	79	68	61	954	1 140
1-4			116	110	73	53	796	1 346
2-1			110	87	68	50	833	1 333
Average			111	92	70	55	861	1 273
1-1	100	0.27	108	90	73	54	1 630	2 670
1-3			102	65	58	51	2 400	2 880
2-7			110	66	55	48	2 535	3 185
Average			107	74	62	55	2 188	2 912
2-2	200	0.53	103	55	53	50	5 440	5 365
2-9			102	56	55	53	5 200	5 410
3-1			108	67	64	59	3 750	4 160
Average			104	59	57	54	4 797	5 145
2-6	500	1.33	100	66	62	59	9 750	10 625
2-8			110	73	72	70	10 125	10 580
3-2			110	67	65	63	8 541	9 250
Average			107	69	66	64	9 472	10 152

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TABLE 2. - SUMMARY OF TORSIONAL BRAID ANALYSIS

EXPERIMENTAL PROCEDURE

Rate of temperature change, $^{\circ}C/min$:	
For temperatures $>25^{\circ}$ C	±3
For temperatures $<25^{\circ}$ C	±1
Atmosphere	Dry nitrogen gas
Drying and curing temperatures, $^{\circ}C$:	
Heated from	25 to 100
Held 1 hr at	100
Heated from	100 to 300
Held 1 hr at	300
Cooled from	300 to 130
Held overnight at	130
Experiment temperature, $^{\circ}C$	130 to -190 to 500 to 25

TABLE 3. - SUMMARY OF TORSIONAL BRAID ANALYSIS RESULTS

Logarithmic decrement loss maxima	Temperature at which loss maxima occurred, $^{\circ}C$	Direction of temperature variation
After drying and curing at 300° C		
γ	-113	Decreasing
	-112	Increasing
β_{H_2O}	-11	Increasing
β	179	Decreasing
α	354	Increasing
Minimum rigidity	377	Increasing
After additional heating to 500° C		
β	179	Decreasing
α	>500	Decreasing

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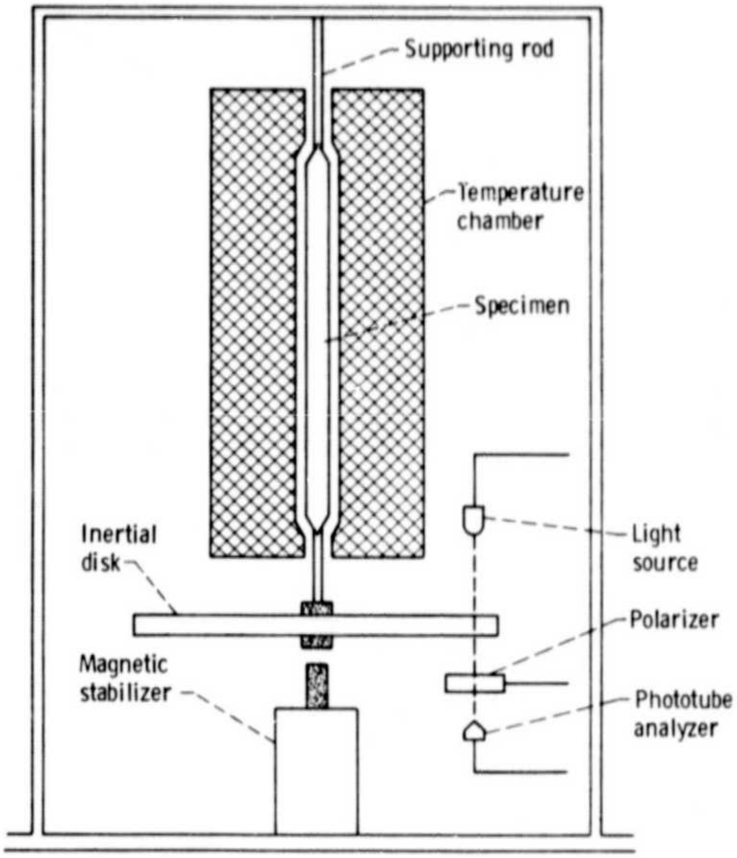

Figure 1. - Typical torsional pendulum apparatus. (From ref. 2.)

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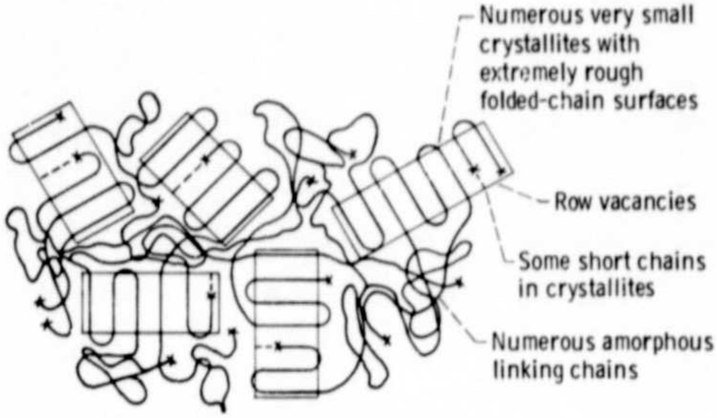
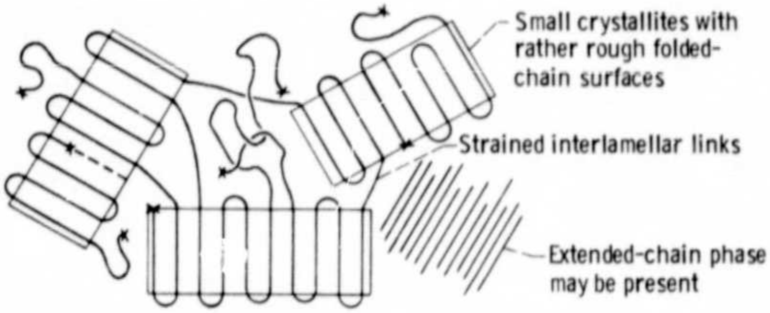
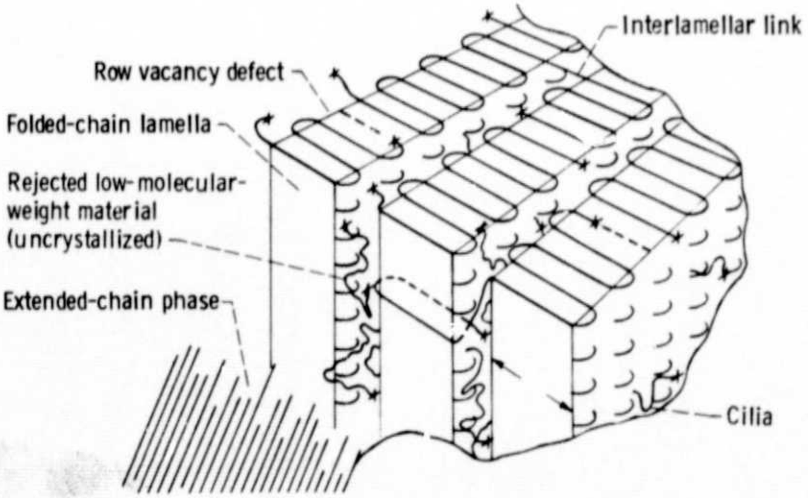


(a) Quench crystallized.



(b) Quench crystallized and annealed.



(c) Isothermally crystallized near melting point.

Figure 2. - Schematic representation of fine structure of a polymer prepared under different crystallization conditions. (From ref. 19.)

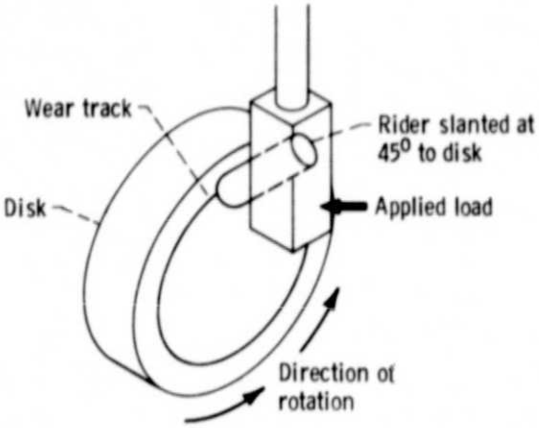


Figure 3. - Schematic diagram of friction apparatus.

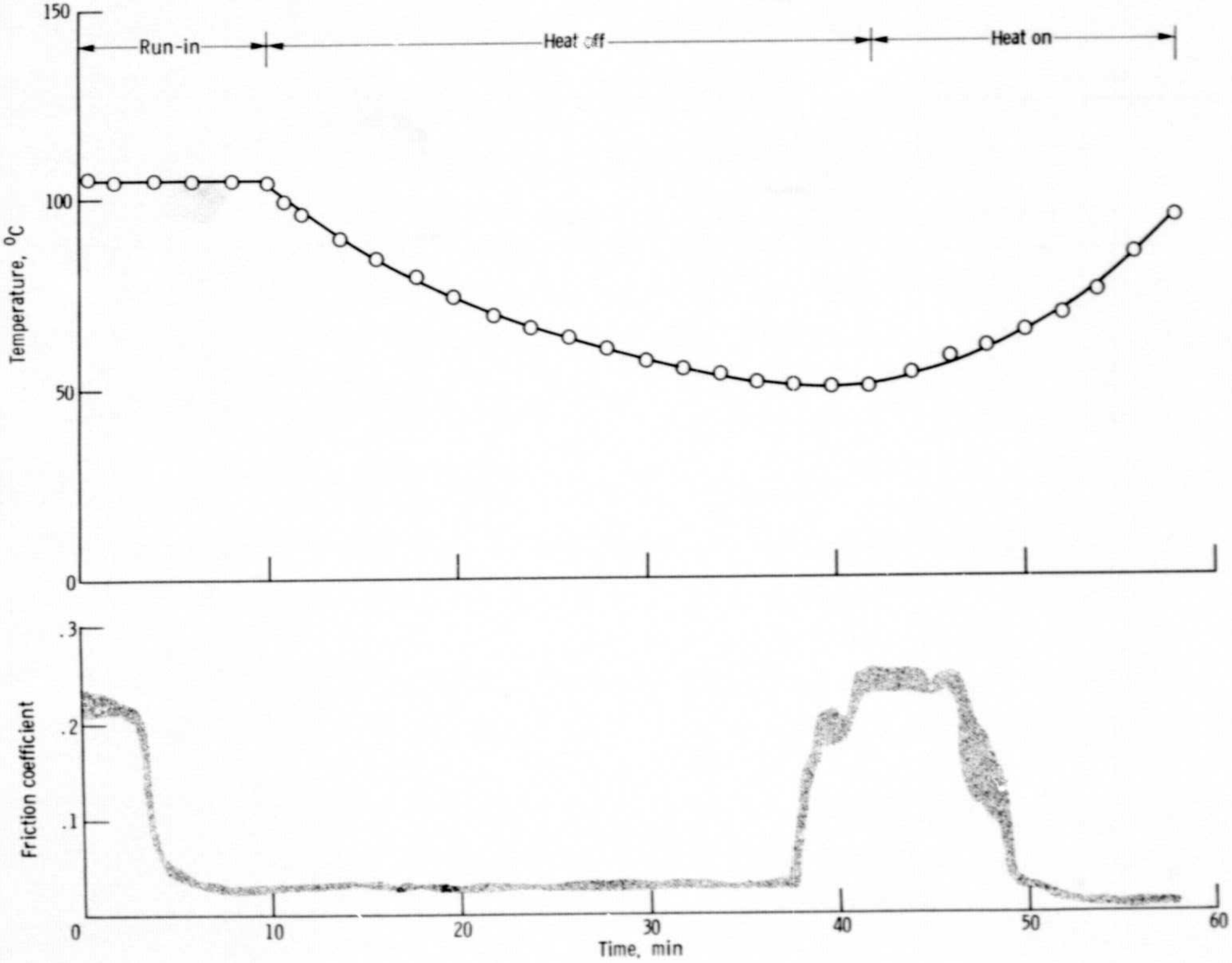


Figure 4. - Temperature and friction coefficient as function of time for a 440C stainless-steel rider sliding on a polyimide film bonded to a 440C stainless-steel disk. Load, 1 kilogram; sliding velocity, 1.6 meters per second (600 rpm); atmosphere, dry argon (10 ppm H_2O).

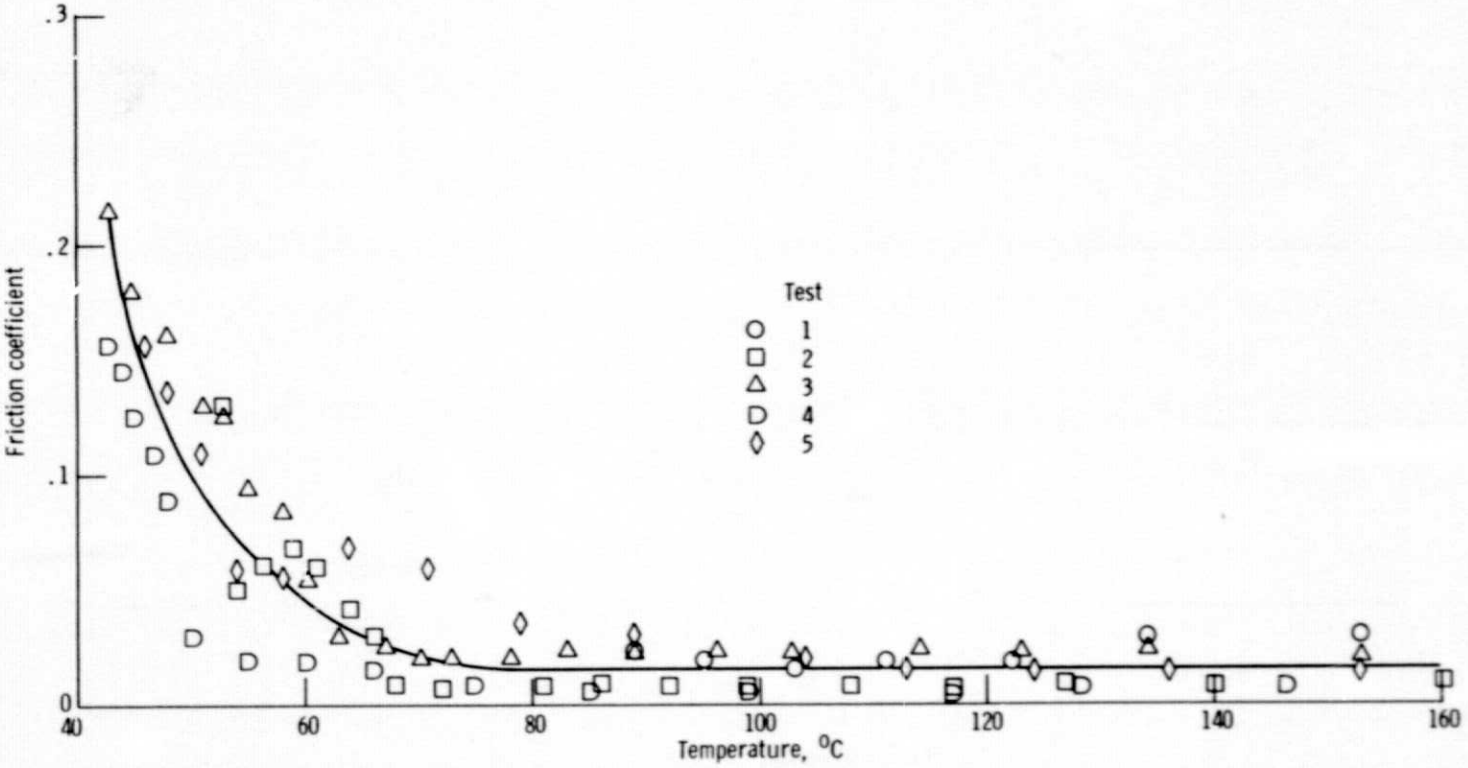


Figure 5. - Friction coefficient as function of temperature for five different tests conducted on polyimide films bonded to 440C stainless-steel disks, illustrating scatter which occurs around friction transition temperature. Test temperature lowered at rate of 3° C per minute; sliding velocity, 1.6 meters per second (600 rpm); load, 500 grams; atmosphere, dry argon (10 ppm H_2O); riders, 440C stainless steel.

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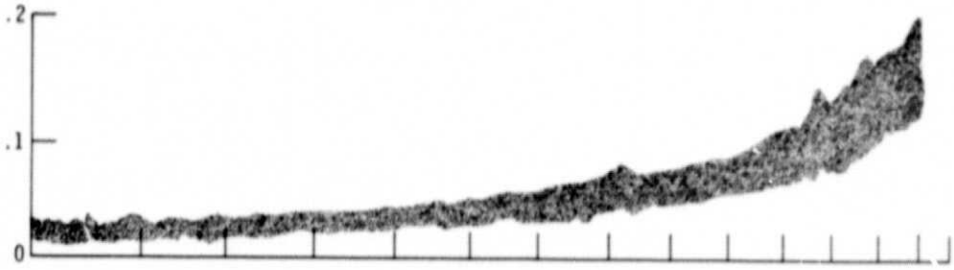
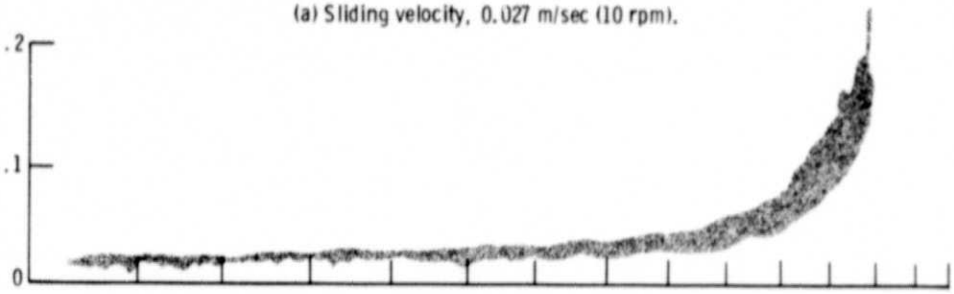
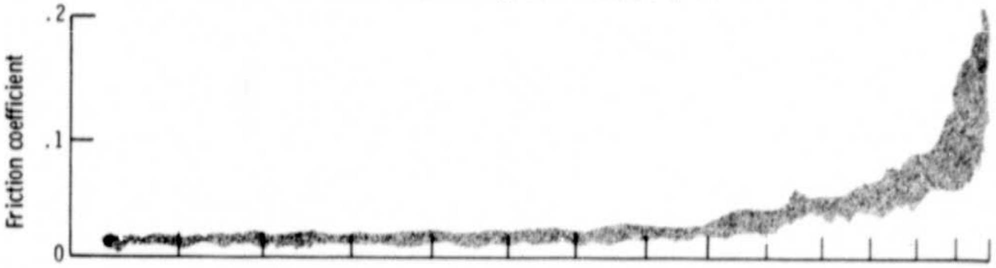


(a) Sliding velocity, 0.027 m/sec (10 rpm).

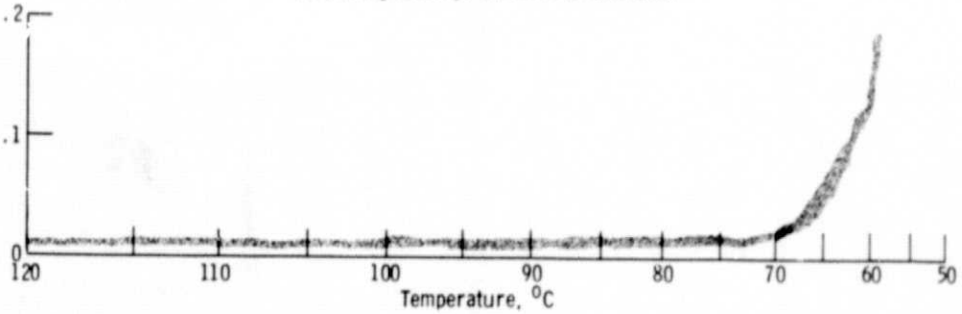


(b) Sliding velocity, 0.13 m/sec (50 rpm).



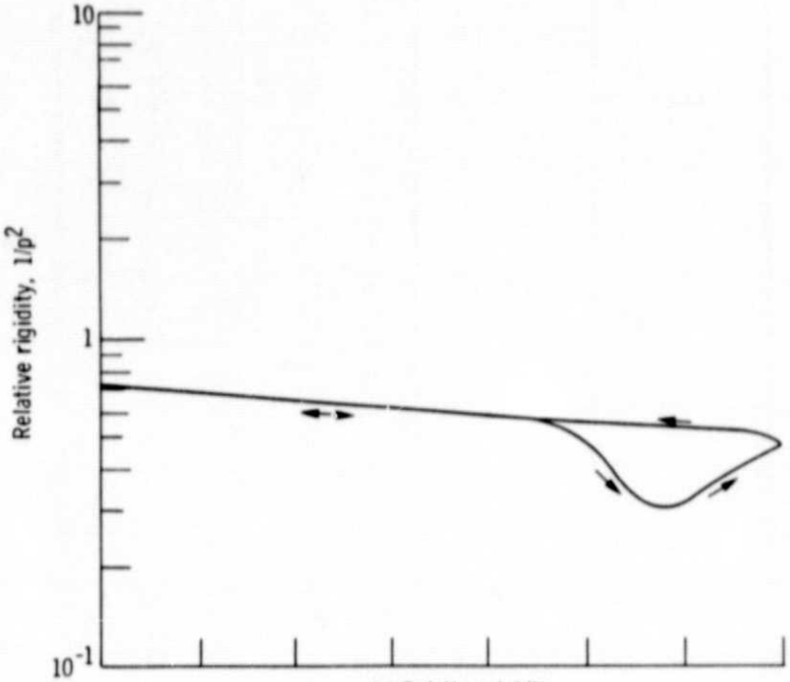
(c) Sliding velocity, 0.27 m/sec (100 rpm).

(d) Sliding velocity, 0.53 m/sec (200 rpm).

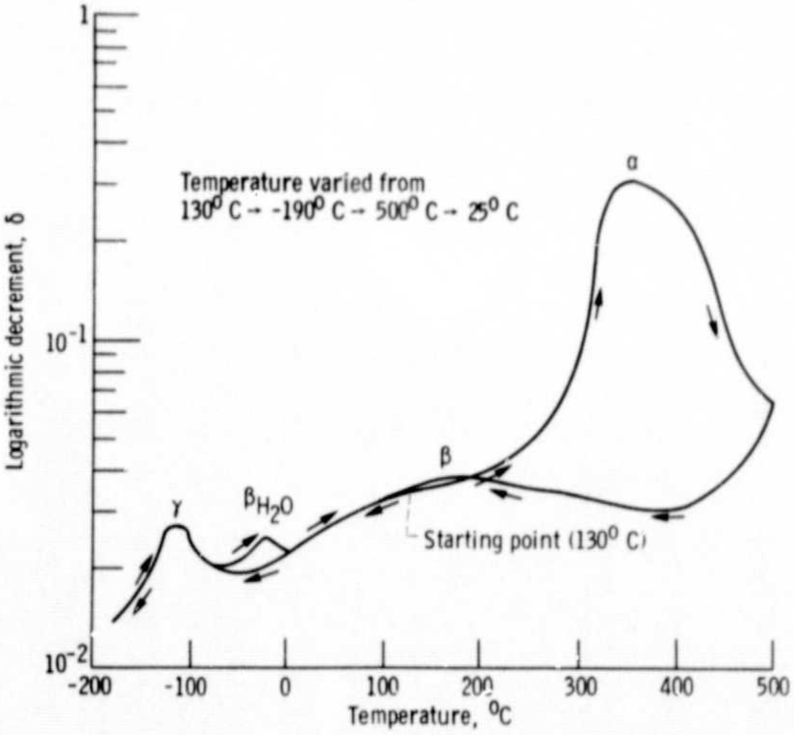


(e) Sliding velocity, 1.33 m/sec (500 rpm).

Figure 6. - Representative friction traces showing effect of velocity on friction properties of polyimide films bonded to 440C stainless-steel disks. Load, 500 grams; atmosphere, dry argon (100 ppm H_2O); riders, 440C stainless steel; wear track diameter, 5.1 centimeters.

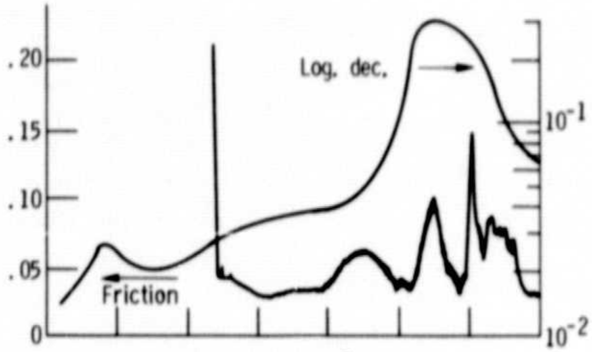


(a) Relative rigidity.

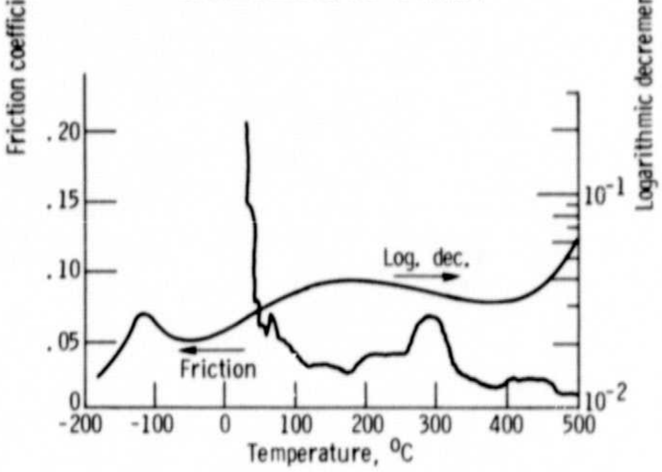


(b) Logarithmic decrement.

Figure 7. - Relative rigidity ($1/p^2$) and logarithmic decrement (δ) for a polyimide (PI-4701) film obtained by the torsional braid analysis technique.



(a) Film cured at 300° C in air.



(b) Film heated in argon to 500° C.

Figure 8. - Comparison of the logarithmic decrement to the friction coefficient of polyimide (PI-4701) films for tests conducted on a (a) film cured at 300° C, and on a (b) film heated in argon to 500° C.

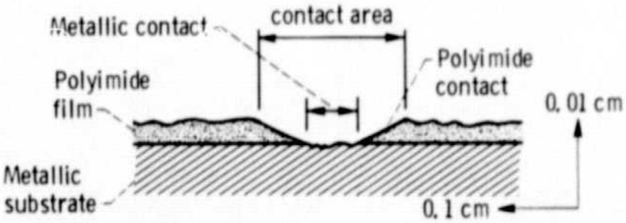


Figure 9. - Schematic representation of the rider contact area on a polyimide coated metal disk, illustrating what happens when the film will not support the rider load under sliding conditions.

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