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POLYPROPYLENE RESILIENCY STUDIES:

DYNAMIC MECHANICAL PROPERTIES OF POLYPROPYLENE, ASBESTOS-FILLED POLYPROPYLENE, AND NYLON 66

Authors: J. A. Faucher
G. M. Bryant
J. V. Koleske

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SUMMARY The mechanical loss, which may be considered as an inverse measure of resiliency, and the components of the complex shear modulus of polypropylene, dyeable polypropylene, asbestos-filled polypropylene and nylon were investigated as a function of temperature with the torsion pendulum. Temperatures ranged from -180 to 240°C. depending on the material investigated. Orientation, annealing, and moisture content when applicable were utilized as variables.

The UCC dye assistant has little effect on the dynamic mechanical properties of polypropylene except at elevated temperatures. Annealing polypropylene improves its properties with the mechanical loss significantly improved (decreased) in the room temperature zone. Oriented specimens showed an increase in mechanical loss with the magnitude of the loss about equal in the orientation direction and normal to it. The glass transition peak of polypropylene was obscured by orientation. The components of the complex shear modulus were increased in and normal to the draw direction, but the increases were markedly different in the two directions.

Dyeable U. S. Rubber, Herculon (melt dyed), and dyeable Shell polypropylene were compared. It was not possible to definitely assign any secondary peaks to the dye or dye assistants. Little difference was found in the overall character of the mechanical loss for these polymers except for the height of the major loss peak. The peak was highest for the melt dyed Herculon and lowest for the dyeable Shell polymer. The Shell and U. S. Rubber polypropylenes had very similar properties in the room temperature zone.

Asbestos filler (Chrysotile) in the amount of 10, 20 or 30% had little effect on the mechanical loss of polypropylene. This filler increased both components of the complex modulus. Moderate annealing times improved the loss and modulus of

Research and Development Department
Chemicals Division
Union Carbide Corporation

asbestos-filled polypropylene. Long annealing times (19 hrs. at 130-140°C.) resulted in poor mechanical properties which have been attributed to a degradation of the polypropylene catalyzed by the Chrysotile. Orientation of the filled polymer increases the mechanical loss and the components of the complex modulus measured normal to the orientation direction. In the orientation direction the shear properties are poorer than those obtained with the unoriented polymer. Young's modulus is largest in the draw direction, and it decreases to a minimal value normal to the draw direction. The highly oriented asbestos-filled polymer is easily fibrillated and may hold some promise as a fibrillating fiber..

Molded Nylon 501 carpet yarn and Zytel 101 (both are nylon 66) were examined and compared with polypropylene. In the room temperature zone dry nylon has far superior loss properties to those of polypropylene. However, when conditioned at constant temperature and humidity, the nylon shows a shift of its major loss peak to the room temperature zone or a new loss peak near room temperature. In the moist conditions employed, which are closer to use conditions than the dry condition mentioned above, the loss properties are about equal to or poorer than those of polypropylene near the temperatures which are important to carpet resilience.

INTRODUCTION The torsion pendulum provides a simple, rapid method for obtaining the mechanical loss, Q^{-1}, and the real and imaginary or loss components of the complex shear modulus of polymeric materials. A torsion pendulum[1] is set into oscillation and it continues to oscillate with a constant frequency and a gradually decreasing amplitude. The log decreament, Δ, is determined from the natural logarithm of the ratio of two successive amplitudes, and from it the mechanical loss can be calculated by means of

$$Q^{-1} = \Delta/\pi. \qquad (1)$$

The mechanical loss is related to the energy stored and the energy lost per cycle by

$$Q^{-1} = \pi \left\{ \frac{\text{Energy lost/cycle}}{\text{Energy stored/cycle}} \right\}. \qquad (2)$$

This, of course, is related to the resilience of a material which may be defined[2] as the ratio of the work recovered to the work absorbed by a deformed material.

With Q^{-1} known it is possible to calculate the real and imaginary components, G' and G" respectively, of the complex shear modulus by the relationships

$$G' = (K/4)f^2\left[4.0 \pm (Q^{-1})^2\right] \quad (3)$$

and

$$G'' = Kf^2Q^{-1} \quad (4)$$

where f is the frequency and K is a constant that depends on the geometry and dimensions of the specimen, the moment of inertia of the system, and certain constants that enter when the differential equation for the motion of the torsion pendulum is solved. The minus sign in the bracket term of Equation 3 is used if the complex shear modulus, G*, is independent of frequency, and the plus sign is used if the dynamic viscosity is independent of frequency. In the work reported on, the dynamic viscosity was assumed to be the frequency independent factor. However, it should be noted that the small values of Q^{-1} encountered with polypropylene result in $(Q^{-1})^2$ being almost negligible compared with 4.0 throughout most of the temperature range covered. From Equations 3 and 4 it can be seen that at small values of Q^{-1} the mechanical loss is given by the ratio of G" to G'. It should be noted at this point that Q^{-1} does not depend on sample dimensions or geometry except in the manner that they affect the frequency; however, both G' and G" do depend on these physical parameters.

In brief, the two components of the complex shear modulus may be thought of in the following manner. When a specimen is loaded in a torsion pendulum, two mechanisms respond to the oscillatory motion. G' comes into being through the distortion mechanisms that respond in phase with the applied load, while G" arises through the distortion that is 90° out of phase with the applied load. These components are related to the complex shear modulus by

$$G^* = \left[(G')^2 + (G'')^2\right]^{1/2} \quad (5)$$

G* was not calculated in this work.

EXPERIMENTAL A recording torsion pendulum similar to that described by Nielsen[1] was used to obtain the mechanical loss as a function of temperature from -180 to 240°C. Various isotactic polypropylenes, nylon 66, ethylene/N-methyl-N-vinyl acetamide (ethylene-MeVA), polyethylene, and asbestos-filled polypropylene were investigated.

Unoriented, unannealed specimens were in an "as molded" condition. This involved molding under pressure near the melting point and then quenching the molded plaque in the press. The plaques were stored at room conditions, unless otherwise noted, for at least 48 hours prior to testing. When specimens were annealed, they were placed in an oven set at the annealing temperature. Unless otherwise noted, at the end of the annealing period the oven was turned off and the specimens were oven cooled to room temperature. Oriented specimens were drawn in an Instron tensile tester to the desired draw ratio. To minimize voiding of oriented specimens, the elongations were carried out at elevated temperatures.

DISCUSSION

Frequency Dependence of Dynamic Mechanical Properties

The mechanical loss, G', and G" are dependent on temperature and on frequency of oscillatory loading. Therefore to fully describe the dynamic mechanical properties of a material, it is necessary to examine both dependent variables and to represent the property-temperature-frequency information in a three-dimensional plot. With the freely oscillating torsion pendulum only the temperature is controlled and the frequency varies with the response of the sample. Thus, what one actually views in a property-temperature plot is a diagonal slice through the three-dimensional plot rather than a true plot at constant frequency. Usually it is assumed that the frequency variation encountered with a torsion pendulum is small, a few cycles over a large temperature range, and does not cause an appreciable shift in dynamic properties. In the case of polypropylene the shift is readily apparent at the temperatures of particular interest in this study.

Since certain data taken with polypropylene on the torsion pendulum seemed anomalous, it was decided to investigate the frequency dependence of Q^{-1}. Specimens of various dimensions and different moments of inertia were used to vary the frequency about one and a half decades over the low frequency range of fractional cycles to almost ten cycles per second. The temperature range of -40 to 60°C., which included the glass transition of polypropylene, was covered. The results for certain temperatures are shown in Figure 1 for Shell Type 5820 polypropylene. Although there is scatter in the data, a noticable dependence on frequency exists. Similar plots were made for G' and G" but are not shown. A less extensive investigation was made with (ethylene-MeVA), and the results are shown in Figure 2. From viewing Figures 1 and 2 it would seem imperative that the frequency be stated along with the values of Q^{-1}, G', G" or Tg for these polymers.

With the frequency dependence of Tg readily available from the above investigation, it was possible to approximate the activation energy for the transition by a method described by Ke[3]. At the point of maximum mechanical loss, i.e., at Tg,

$$\tau\omega = 1 \qquad (6)$$

where τ is the relaxation time and ω is the angular frequency in radians per second. This method assumes that a single relaxation time exists. Since the temperature dependence of the relaxation time is represented by

$$\tau = \tau_o \exp(\Delta H/RT), \qquad (7)$$

where ΔH is the activation energy, R the gas constant, T the absolute temperature, and τ_o a constant, it is a simple matter to calculate τ from Equation 6 and make the Arrhenius type plot implied by Equation 7. This plot is shown in Figure 3 for Shell 5820 polypropylene and for ethylene-MeVA. The activation energy of 40.6 kcal. per mole for polypropylene is in the neighborhood of the 47.3 kcal, per mole obtained for the stress relaxation process[4] with dyeable Shell 5820 polypropylene.

Polypropylene

Samples of Shell Type 376 and 5820 and Hercules Type 6420 polypropylene with and without the UCC dye assistant (10% of the ethylene-MeVA copolymer) were examined. The results for the Shell Type 376 are shown in Figures 4 and 5. Near room temperature, which is of importance to carpet resiliency, the mechanical loss was little affected by ethylene-MeVA. Above 30°C. the ethylene-MeVA causes an increase in the mechanical loss except in the case of the Shell Type 5820 polymer, not shown, which had about equivalent loss with and without ethylene-MeVA until temperatures of about 120°C. were reached. By examining the frequency, Figure 4, it can be seen that the lower frequency and with the dyeable polypropylene would cause the results to be somewhat high (also see Figure 1). If a correction for the frequency difference were made, the curves would have better agreement. The general character and magnitude of G' and G" are not significantly altered by the ethylene-MeVA as shown in Figure 5.

If two polymers had quite different glass transition temperatures, they would be considered incompatible if both loss peaks were apparent when examining a mixture of the materials. If a single loss peak were obtained for the mixture, the polymers would be considered compatible. The loss character of ethylene-MeVA is compared with that of the polypropylene and dyeable polypropylene in Figure 4, and it is readily apparent that the polymer

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has a pronounced loss peak at about 0°C. (Here the frequency dependence is such as to exaggerate the loss differences.) Unfortunately, the loss maximum for both polypropylene and EMeVA occurs at about 0°C., which does not allow a great deal to be said about the compatibility of the materials.

Molded plaques of polypropylene were annealed following the schedule shown in Table I. The mechanical loss data for the Shell Type 376 polypropylene are shown in Figure 6.

TABLE I

ANNEALING SCHEDULE AND PROPERTIES OF POLYPROPYLENE
(ALL ANNEALED SAMPLES WERE OVEN-COOLED)

Type Polypropylene	Annealing Time, min.	Annealing Temp., °C.	Density	(Loss Max.) Tg °C	Frequency at 0°C., c.p.s.
Shell 376	0	---	0.9108	8	4.7
Shell 376	80	120-130	0.9156	3	2.2
Shell 376	180	130-140	0.9206	3	2.3
Shell 302	0	---	0.9166	7	5.0
Shell 302	300	130-140	0.9226	5	2.7
Shell 5824*	0	---	0.9084	2	2.1
Shell 5824*	1200	130-140	0.9112	2	2.4

* Shell Type 5824 contained a nucleating agent.

As expected, the value of Tg was not significantly affected by annealing (the higher Tg values shown in Table I for the unannealed samples are probably due to the measurements being made at a higher frequency than for the annealed samples). Above Tg there is a marked decrease in loss for the annealed samples indicating that the materials are more resilient until elevated temperatures are reached. Although the spectrum of frequencies is not shown, the unannealed specimen was run at higher frequencies than the annealed specimens which results in the values being somewhat low for direct comparison. Except for the introduction of secondary loss maxima, annealing has little effect below Tg. No attempt will be made to explain these secondary peaks, except to say that it is unlikely that they are caused by oxidation.

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The calculated values of G' and G" for the annealed Shell Type 376 are shown in Figures 7 and 8. The position of the maximum in G" is unchanged by annealing, although the value of Tg has decreased slightly, as would be expected, from that obtained by the mechanical loss data. Above Tg a plateau region becomes more prevalent as the annealing time is increased. This probably is due to an increase in crystallinity or a perfection of crystallities effected by annealing. Below the Tg region, G" is affected in a more complex manner than it is above Tg. At the shorter annealing time G" is increased and at the longer time it is decreased. Here again the secondary peaks are apparent. Values of G' are increased by annealing as would be expected; however, in the region of Tg the increase is very slight. Below Tg the effect of annealing time is similar to that found for G" although it is quite possible that the difference between the two annealed samples is within experimental error. As previously noted, the sample size and shape are taken into account in calculating G' and G", and thus the values obtained at high temperatures may be in error due to a change in one of these parameters. Overall, it can be concluded that annealing does enhance the resilience of polypropylene in the temperature zone important to carpet use and at temperatures above Tg.

To obtain an insight on the effect of nucleating agents, Shell Type 5824 polypropylene (melt flow 13.8), which contained a nucleating agent added by Shell, was examined in an as molded condition and after annealing. The results were then compared to those obtained with Shell Type 5820 polypropylene (melt flow 11.5) which supposedly was very similar to 5824 except that it did not contain a nucleating agent. The mechanical loss and appropriate frequencies are shown in Figure 9. Since these results are taken at almost the same frequencies, they are directly comparable. Before annealing, the nucleated polypropylene, density 0.9084, is somewhat less resilient than the non-nucleated polymer, density 0.9242. However, after annealing for 20 hours at 130-140°C., the nucleated polymer, density 0.9112, has a marked decrease in mechanical loss above Tg indicating that there should be improved resilience in and above the room temperature zone. The temperature dependence of G' and G" shown in Figure 10 indicates that the decreased loss of the annealed, nucleated polypropylene is brought about principally by a large decrease in the loss component along with a smaller increase in the real component of the shear modulus (see Equations 3 and 4).

Since orientation effects were thought to be of significant importance to resiliency, several oriented specimens were examined and a typical example is discussed. Shell Type 5820 polypropylene was molded and a plaque was drawn 9:1 at 105°C. The density before orientation was 0.9242 and after

orientation was 0.9092 indicating that some voiding occurred during orientation. Measurements of the loss and frequency are shown in Figure 11. For the oriented polymer the shearing force was applied both normal to the draw direction (specimen mounted in the apparatus parallel to the draw direction) and parallel to the draw direction (specimen mounted normal to the draw direction). From Figure 11, it can be seen that the loss is greater for the drawn specimens. To compare the curves at equivalent frequencies, the curve for the unoriented polymer would be shifted to slightly higher loss values throughout most of the temperature range investigated. The increase in loss after orientation may be due to the presence of voids in the drawn polymer. It should be noted that little difference exists in the magnitude of the loss for the oriented polymer in the two directions except between 80 and 110°C.

Both components of the complex shear modulus, in each of the directions examined, are markedly increased by drawing as shown in Figures 12 and 13. At 0°C. and 20°C. the magnitude of G' and G" are about 10-20 times greater normal to the direction of orientation and about 2-3 times greater parallel to the direction of orientation than those of the unoriented polymer. The character of the properties is significantly altered by orientation in all instances, though not in the same manner, except for G' of the polymer parallel to the draw direction which retains a resemblance to G' of the unoriented polypropylene. Although there is considerable variation in the magnitude and character of the properties of polypropylene when oriented, the mechanical loss or ratio of the components of the complex shear modulus in the two directions is nearly the same.

It is possible to attempt an explanation for the magnitude of the changes in the complex shear modulus. The oriented polymer has its molecular chains oriented to a greater degree parallel to the draw direction. When the shearing force is applied normal to the draw direction the primary bonds of the polymer chains are in a position to resist the force to a greater degree than they did in the unoriented polymer with the result being a very marked increase in modulus. When the shearing force is applied parallel to the draw direction the weaker secondary bonds between the chains become the force resisting components. In this latter case one would expect a lower modulus than that obtained for the unoriented polymer. However, it is possible that the order, and therefore cooperative secondary bonds, created by orientation is more important than the contribution of the chains or chain segments aligned in any given direction in the unoriented polymer. That is, the orientation creates cooperative secondary bonds that have a larger force resisting capacity than the random secondary bonds

and primary bonds that exist in any direction in the unoriented polymer. This latter factor would allow for an increase in modulus, as was obtained in this instance, in the parallel direction even though the secondary forces come into play to a greater degree than do the primary bonds.

It is interesting to note that Wakelin, et. al.,(5) who examined the torsional, stress-strain, and bending moduli of nylon 66 and Dacron filaments, found that while the stress-strain and bending moduli showed marked increases with increasing draw ratio, the torsional modulus was only slightly increased by drawing. To account for this difference, it was thought that the drawing process may increase the torsional modulus near the core of the filament and has little effect on the modulus of the material near the surface. Since the specimens used in the work being reported on were entirely oriented and no torsion measurements were made on filaments, it is not possible to substantiate or to refute this theory. The manner in which a polymer in a carpet responds to the various forces applied during normal, everyday use probably encompasses all of these moduli in a complex fashion.

Recently U. S. Rubber Company announced a new dyeable polypropylene and Hercules Powder Company has been marketing a melt-dyed polypropylene under the trade name Herculon. Yarns of these two materials were molded into plaques and examined with the torsion pendulum to see if the added materials affected the dynamic properties in any significant manner. The results were compared to those obtained with dyeable Shell Type 5820 polymer and are shown in Figure 15. The frequencies are about equivalent for the three polymers so the results may be directly compared.

In general, there is little difference in the overall character of the mechanical loss for these three polymers. The Shell polymer has the best overall properties, but in the room temperature zone which is important to carpet resilience there is no difference between the Shell and U. S. Rubber polymers. The height of the glass transition peak shows marked differences. How this would affect the final properties of the polymers is not known; however, it seems probable that the lower the peak value, the more resilient will be the final product. There is an indication of a secondary transition at about -60°C. with the Herculon that may be due to the melt-dyeing agent, but this is very slim evidence. In addition, sometimes polypropylene shows a peak at about this temperature as shown in Figure 6. The U. S. Rubber polymer has a definite peak at 80°C., but it does not seem reasonable to assign this to the dye assistant which supposedly is of low molecular weight. Here again, some

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polypropylenes show a small peak or inflection point at about 70°C. that has been attributed to the onset of crystallite melting.

Asbestos-Filled Polypropylene

To determine the effect of a filler on resilience, blends of Shell Type 5820 polypropylene containing 10, 20, and 30% asbestos fiber were prepared by milling the two materials at 165-170°C. for 5-10 minutes. The asbestos used was chemically refined, Grade 7 Chrysotile obtained from the Nuclear Division. The asbestos appeared to be well dispersed in the milled mixture; but when plaques were molded, the 20% and 30% asbestos blends had a high concentration of asbestos near the edge and center of the plaque. Twenty per cent of the filler increased the density from 0.9242 to 1.039.

The mechanical loss data shown in Figure 16 indicated that the filler has little effect on the resilience of polypropylene except at elevated temperatures. The 20% blend appears to have the best characteristics above room temperature; however, it should be kept in mind that the asbestos was not well dispersed in this sample and the concentration of filler is only approximate. In addition, the data for the 20% blend was taken at frequencies that were about 20% higher than the other filled polymers which would have the effect of decreasing the loss values. The Tg was not changed by addition of filler, but there is evidence of a secondary loss peak in the 80-110°C. temperature range. (Note: Hercules Powder Company recently placed an asbestos-filled polypropylene, Pro-fax 66F1, on the market for use in extrusion and injection molding applications. Their material is said to retain or augment several desirable properties of unmodified polypropylene. From certain properties listed in the data sheet[6], it would seem that they use Crocidolite rather than Chrysotile for the filler.) The values of G' and G" are shown in Figure 17. The real component is increased by increasing the filler content except for the 20% blend which shows a lower modulus below room temperature. Only the 30% asbestos blend shows pronounced effects of the filler. Since the asbestos filler should have good mechanical loss properties but did not enchance those of polypropylene, it is quite possible that the filler inhibited perfection of crystalline regions or crystallization of the polymer. Thus the loss improvement obtained from addition of filler is balanced by an increase in the amorphous character of the polypropylene.

To test the postulation that the filler inhibited the crystallization of the polymer, specimens of the 20% blend were annealed at 130-140°C. for 2.5 hours and for 19 hours. The density after 19 hours annealing was 1.081 compared with 1.039 for the unannealed filled polymer. There was insufficient 2.5 hour material for a density determination. The surface of the specimen annealed for 19 hours was crazed. Viewing the cross section of this specimen revealed a thin cream colored perimetric region that seemed to be quite porous. This specimen was brittle and poor in strength properties.

The mechanical loss measurements are shown in Figure 18. The moderately annealed material has improved resilience as indicated by the generally lower mechanical loss. The glass transition temperature has been shifted to a lower temperature and the possibility of a secondary loss peak near 110°C. still exists after annealing. The long annealing time produced a marked increase in Q^{-1} and a much less resilient material in the temperature range investigated than the unannealed or moderately annealed filled polymer.

The components of the complex shear modulus are shown in Figure 19. The real component increased for the moderately annealed specimen and severely decreased for the 19-hour annealed specimen. The imaginary component decreased with annealing time. Since Q^{-1} is related to the components of the complex modulus by $Q^{-1} = G''/G'$, the decrease in G'' is not sufficient to compensate for the decrease in G' for the 19 hour specimen and much poorer resilience resulted.

Since moderate annealing improved the mechanical properties, the initial postulate seems to be confirmed. The effect caused by long annealing times is evidentally a severe degradation of the polypropylene. In a recent Avisun Corporation patent[7], it is shown that asbestos in all forms except Anthophyllite in the presence of particular inhibitors catalyzes the heat degradation of polypropylene.

The 20% asbestos fiber blend was drawn 4:1 and 12:1 at 145-155°C. in an Instron tester and examined with the recording torsion pendulum. The density decreased from 1.039 for the unoriented material to less than 0.804 (the limit of the density gradient used) for the oriented materials. The mechanical loss properties are shown in Figure 20. Orientation has little effect on the glass transition temperature except for a slight decrease with the 12:1 draw-ratio material. Below Tg the loss increases with increasing orientation, but above Tg the increase in loss is independent of draw ratio except for the 4:1 and 12:1 draw ratio materials tested normal to the draw direction at the higher temperatures where a possibility of a secondary transition exists. In the orientation direction the loss is

higher than it is normal to it throughout the temperature range investigated. The increase in loss with orientation is not too surprising when one considers that a large amount of voiding must have taken place on orientation to account for the extreme decrease in density. The voids probably act as amorphous material which causes an increase in loss at any given temperature. It is quite certain that annealing the oriented specimens would decrease their mechanical loss. The frequencies have been noted at two temperatures in Figure 20, and it should be kept in mind that this difference in frequency is such as to accentuate any real differences in the materials being compared.

The components of the complex shear modulus normal to the draw direction are shown in Figure 21. The real component increases with increasing orientation except for the unexpected decrease above 40°C. for the 4:1 draw-ratio material. The imaginary component increases with increasing orientation. In addition, the G" curve for the 12:1 drawn material shows evidence of several secondary loss peaks. The marked increase in complex modulus with orientation seems quite dramatic when one considers that the increases came about even though the density of the material decreased about 20% on orientation.

Figure 22 shows the components of the complex shear modulus in the direction of orientation and normal to it for the 12:1 drawn material. As discussed above G' and G" are increased normal to the draw direction on orientation as one would expect. In the draw direction G' has a very low value and G" is increased below the vicinity of Tg and decreased above the vicinity of Tg. Thus it seems that the secondary bonds in the direction of orientation are weak and in large part their formation or perfection may have been inhibited by the presence of the asbestos. These highly oriented filled materials were easily fibrillated and may hold some promise as a fibrillating fiber that contains hydrophilic and hydrophobic groups. R. G. Curtis attempted to dye the asbestos in a 5 mil. plaque of the 20% blend and had good success with 2% Celliton Fast Red, GGA. However, little or no dyeing took place with 2% Zylene Milling Blue, GL, with 4% sulfuric acid or with 2% Calcodin Blue, 4 GL, with 20% sodium chloride.

Utilizing specimens of the 20% blend that had been drawn 8:1 at 160°C., Young's modulus was determined from stress-strain data at room temperature to be 1.3×10^{10} in the draw direction, 0.33×10^{10} at 45° to the draw direction and 0.13×10^{10} dynes/cm^2 normal to the draw direction.

Nylon 66

Nylon performs well as a carpet yarn, as evidenced by its rapid growth in this textile application. For this reason its dynamic mechanical properties were examined and used as a reference material of good resiliency. Zytel 101, a molding grade of nylon 66, was used for most of the investigation. Textured Nylon 501 carpet yarn, nylon 66, that had been molded into a plaque has essentially the same properties as Zytel 101. Since nylon is moisture sensitive, it was examined at various moisture contents. Dry nylon, 0% humidity, was obtained by drying the plaque in a desiccator over anhydrous $CaSO_4$ for at least 48 hours prior to use. Since dry nitrogen at various temperatures is used as a heat transfer agent in the torsion pendulum apparatus, the dried specimens should have remained at low moisture contents throughout the runs. Nylon was also conditioned at constant temperature and humidity (73.4°F. dry bulb and 61.6°F. wet bulb) for two weeks prior to measurement. Below 0°C. the dry nitrogen heat transfer agent should have had little effect on the moisture content of the conditioned nylon, but above 0°C. undoubtedly some loss of moisture took place. The 100% relative humidity conditions were obtained by suspending the nylon specimen over water in a closed system at room temperature for 24 hours prior to use. Below 0°C. no attempt was made to control the humidity of the heat transfer agent, but above this temperature the dry nitrogen was bubbled through water before being sent to the mounted specimen.

The mechanical loss of dry nylon 66 is compared with that of polypropylene in Figure 23. The loss curves show the three characteristic loss peaks associated with nylon and the single peak associated with polypropylene. Near room temperature dry nylon has extremely low loss implying a high degree of resiliency. However, if Figure 24, which shows the loss curves for nylon at various moisture contents, is examined, one finds a different behavior. The loss curves for nylon in the presence of moisture have been significantly altered in the room temperature zone. This alteration is such that nylon now has about the same or higher loss than polypropylene. Thus under conditions that would be more similar to room conditions (the constant wet and dry bulb conditions) the nylon is no better than polypropylene in an "as molded" state. Of course, the effect of orientation and/or annealing on properties at various moisture contents may have an important influence on a final product as nylon carpet yarn. In addition, the texturing method used on a particular yarn may significantly alter some or all properties studied from a basic standpoint.

Under the constant temperature and humidity conditions, Figure 24, it would seem that nylon has been plasticized, for the major loss peak that occurred at about 70°C. in the dry nylon has shifted to a temperature of about 20°C. This behavior is similar to that reported by Woodward, et. al.,[8] for nylon 66 held at 100% relative humidity for 3 weeks except that the height of the peak was increased in their work. The odd behavior, indicated by the short plateau between 30 and 60°C., of the loss for the conditioned specimen may be due to a change (decrease) in moisture content which could become appreciable in this temperature range. The lowering of the moisture content with temperature is verified by the fact that the conditioned specimen's loss curve approaches that of the dry nylon at the higher temperatures.

The curve for nylon at 100% relative humidity shown in Figure 24 indicates a different behavior. A new peak is apparent at about 0°C. and there has been only a slight shift in the major loss peak. It should be kept in mind that in this instance the specimen was not dried by heat transfer agent since moist nitrogen was used above 0°C. These differences can be seen more clearly in Figure 25 which shows the imaginary portion of the complex modulus.

Although the data presented on the effect of water on nylon are meager, some attempts at explanation of the phenomena can be made. It is possible that a stoichiometric relation exists between water and nylon before plasticization takes place. Severe deviations from the proper ratio result in the water and nylon acting independently. Of course without more data, an explanation such as this is only speculation. Another possibility could be that the slow drying caused by the heat transfer agent in the case of the constant dry and wet bulb conditioned nylon produced an apparent blending of the two separate peaks that were observed with the 100% relative humidity specimen. This possibility would be more secure if the short plateau region (30-60°C.) extended to higher temperatures, say about 100°C. A third way of looking at the data is to assume that unbound water was present in the 100% relative humidity conditioned specimen and melting of ice at 0°C. caused the secondary loss peak (here the possibility would exist that the unbound water had been vitrified and one observes the devitrification and subsequent melting of icé in this region). However, although this may seem plausible, one must keep in mind that the nylon was not "wet to the touch" and it should take a relatively large amount of unbound water melting or devitrifying to cause the distinct peak seen at 0°C. Actually the work of Woodward, et.al.,[8] does not help in these explanations, for there was no mention of whether or not humidity conditions were controlled during the time their data was taken.

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A specimen of molded Nylon 501 carpet yarn was oriented to a draw ratio of 3.5:1 in an Instron tensile tester at 220-225°C. The oriented specimen was examined only by applying the shear stress normal to the orientation direction. The results shown in Figures 26 and 27 are in general agreement with those obtained with polypropylene. The mechanical loss and the components of the complex modulus increase when the specimen is oriented. It should be mentioned that Marlex 6050 (polyethylene) was also examined in an as molded and in an oriented state and similar results were obtained.

NOTEBOOK REFERENCES:

5614-JVK; 29 through 35-JEP; 37, 38, 39-JEP

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Joseph V. Koleske

jdm

ATTACHMENTS
27 Figures

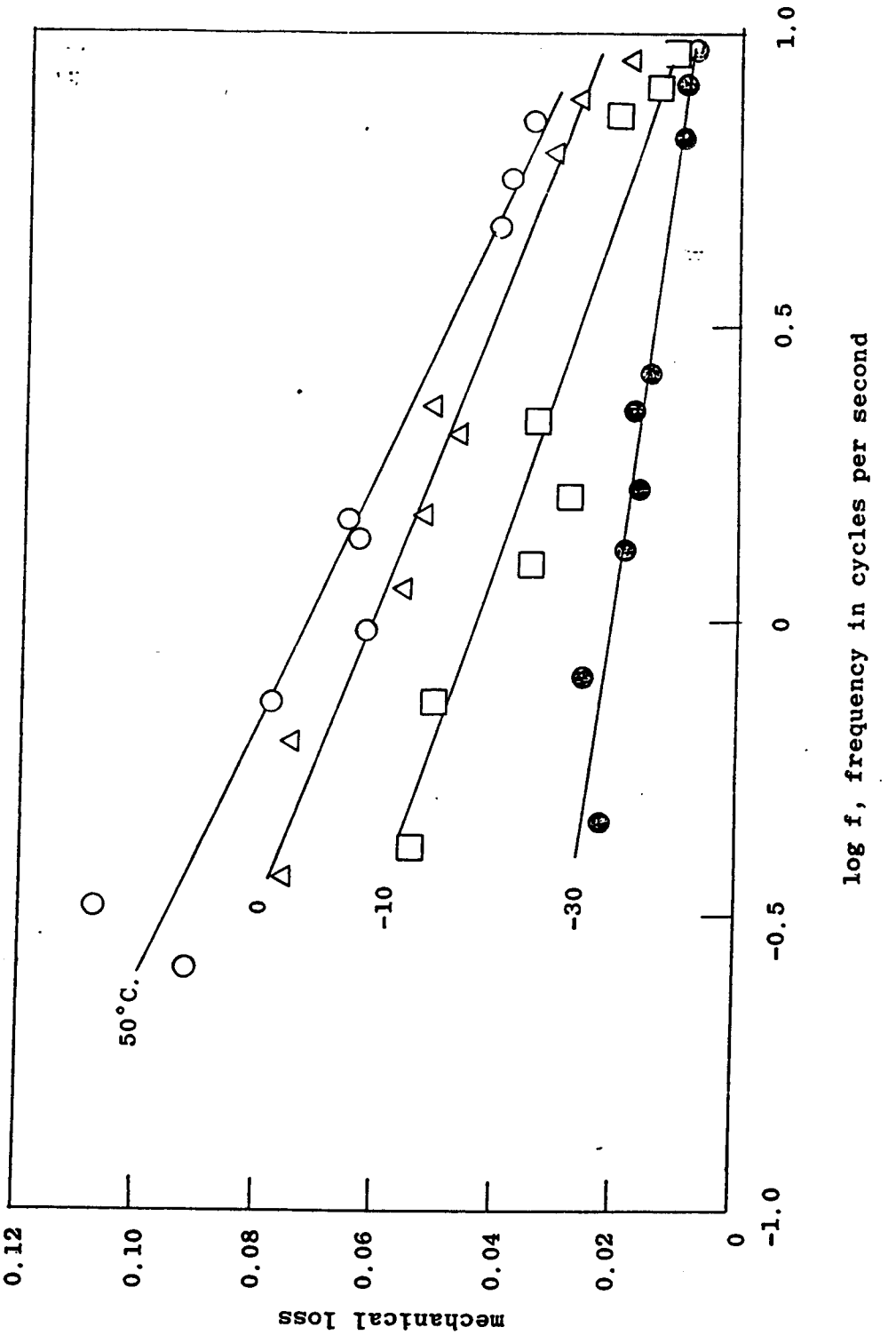


FIGURE 1. FREQUENCY DEPENDENCE OF THE MECHANICAL LOSS OF SHELL 5820 POLYPROPYLENE.

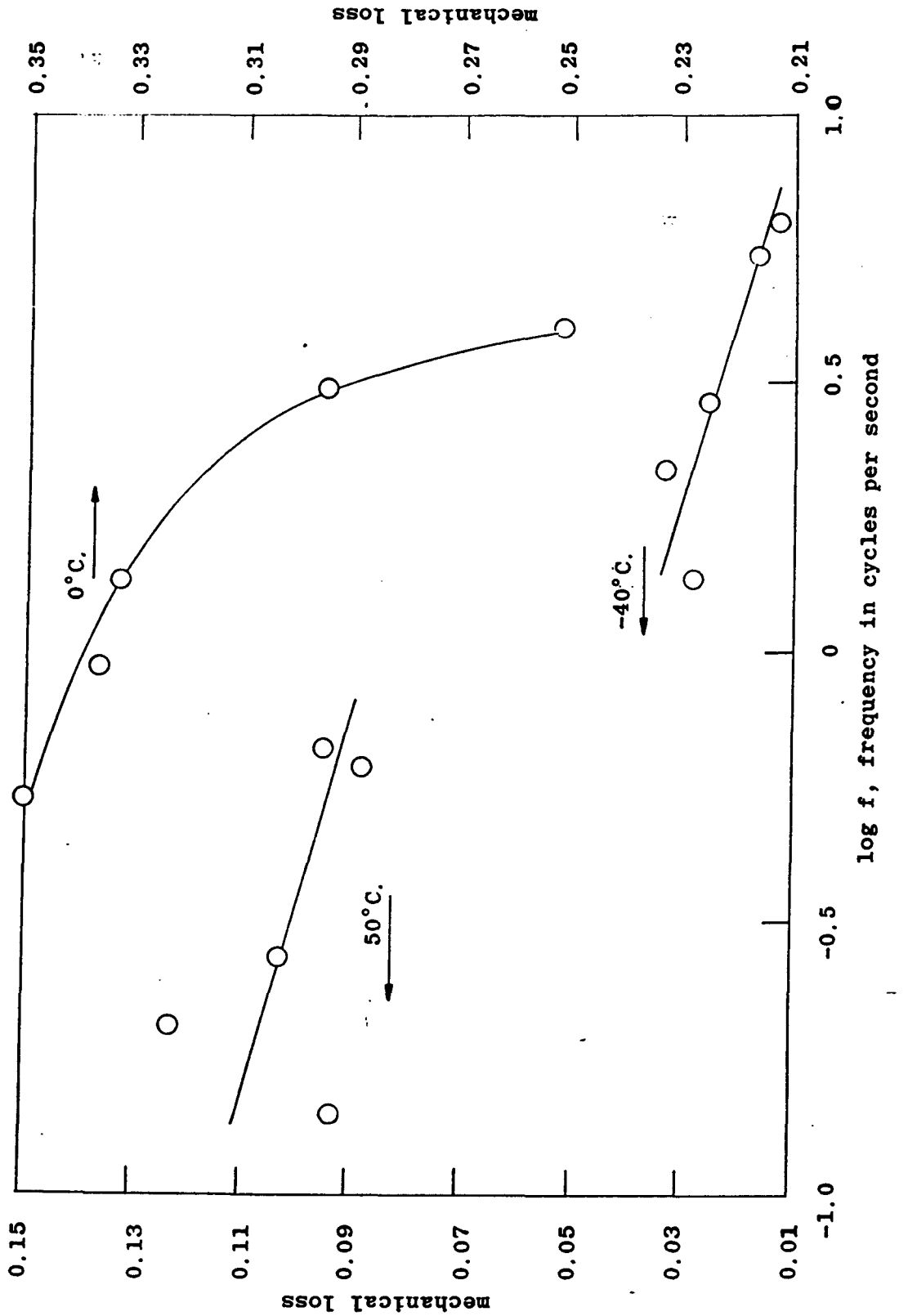
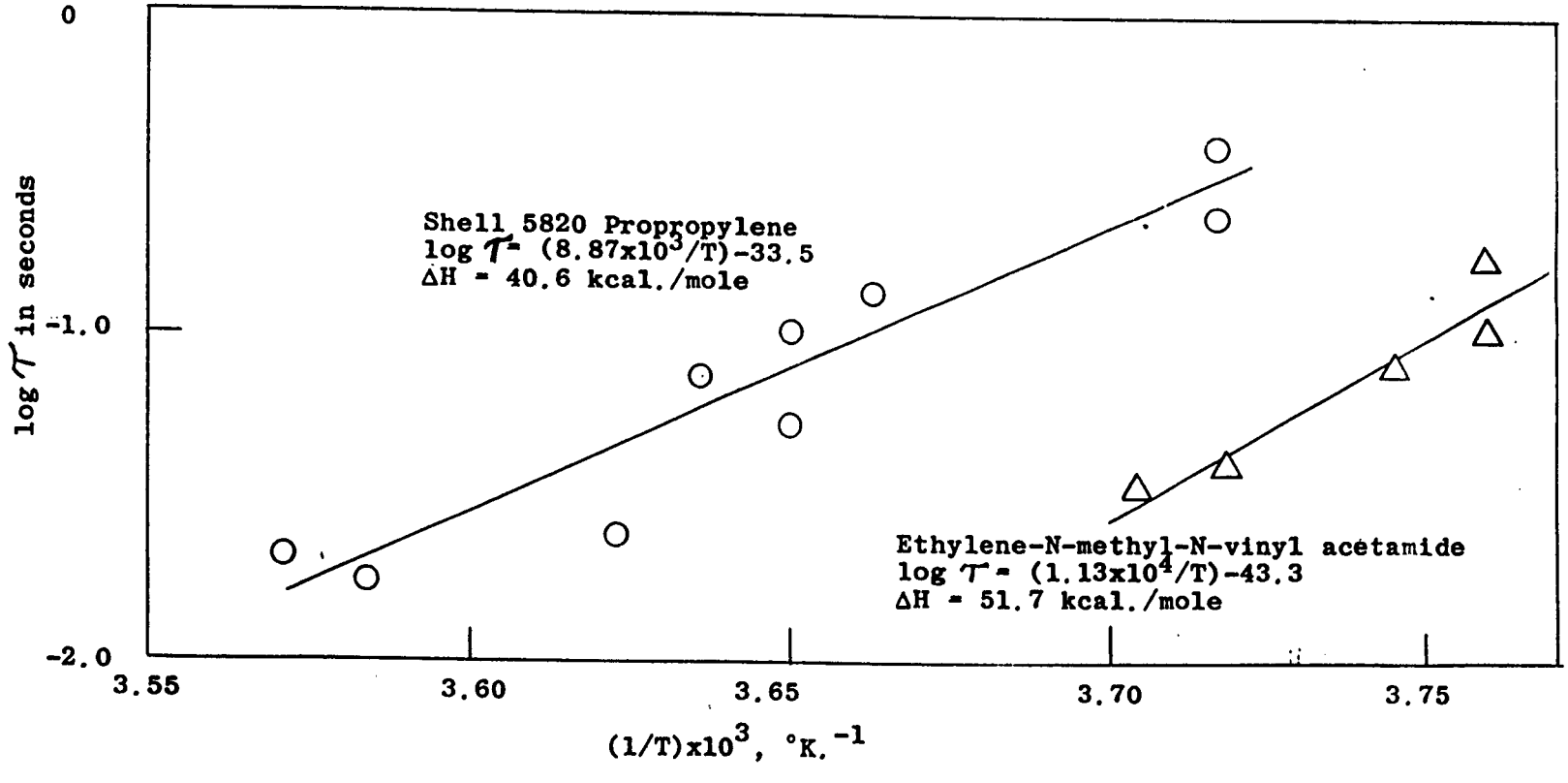


FIGURE 2. FREQUENCY DEPENDENCE OF THE MECHANICAL LOSS OF ETHYLENE/ N-METHYL-N-VINYL ACETAMIDE (LOT 1433, STIRRED AUTOCLAVE)

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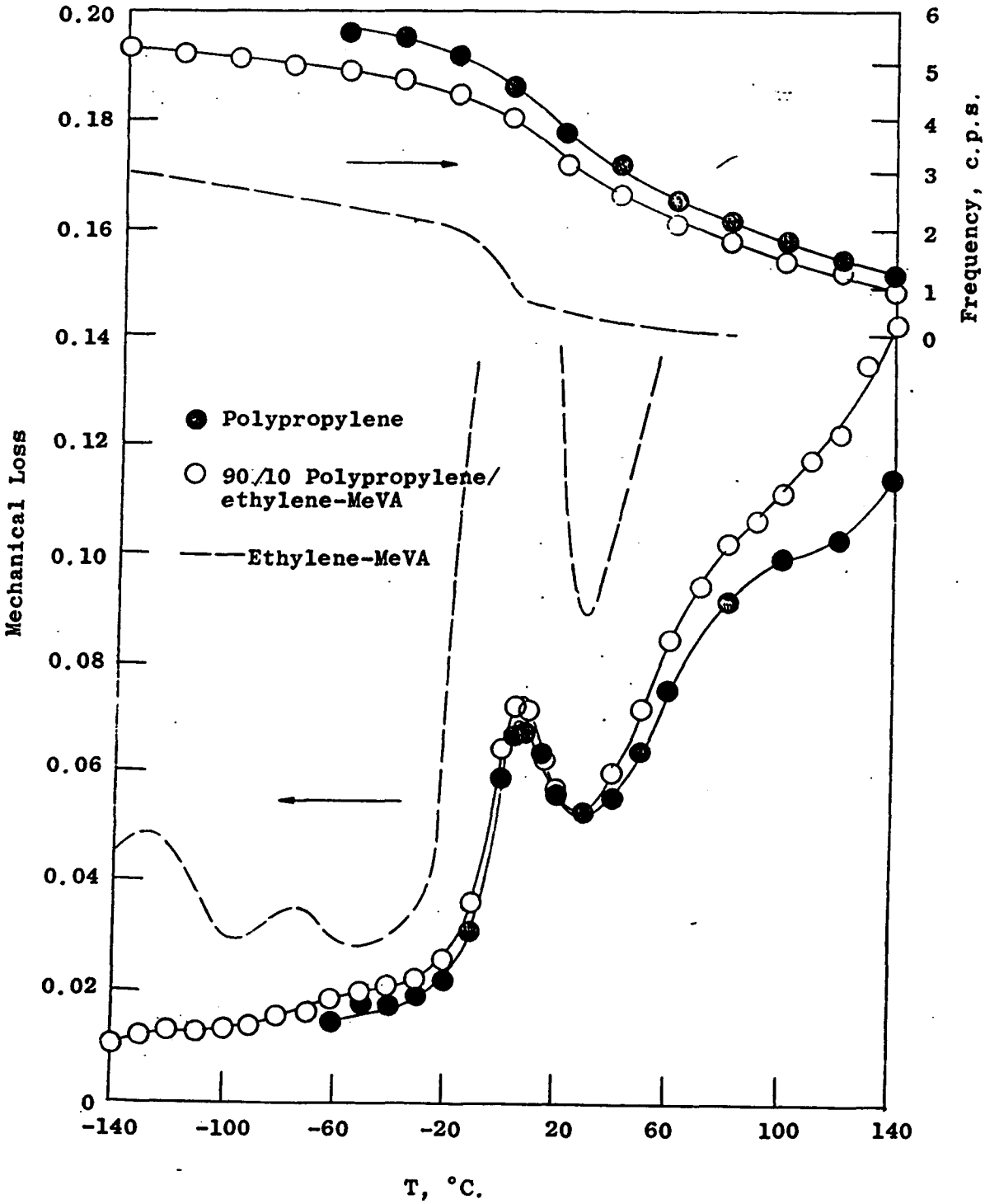
Union Carbide trial exhibit UC-4754: J. A. Faucher, G. M. Bryant and J. V. Koleske, Polypropylene Resiliency Stud...
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FIGURE 3. ARRHENIUS TYPE PLOT FOR POLYPROPYLENE AND ETHYLENE/N-METHYL-N-VINYL ACETAMIDE. LINES REPRESENT A LEAST SQUARES FIT OF THE DATA.



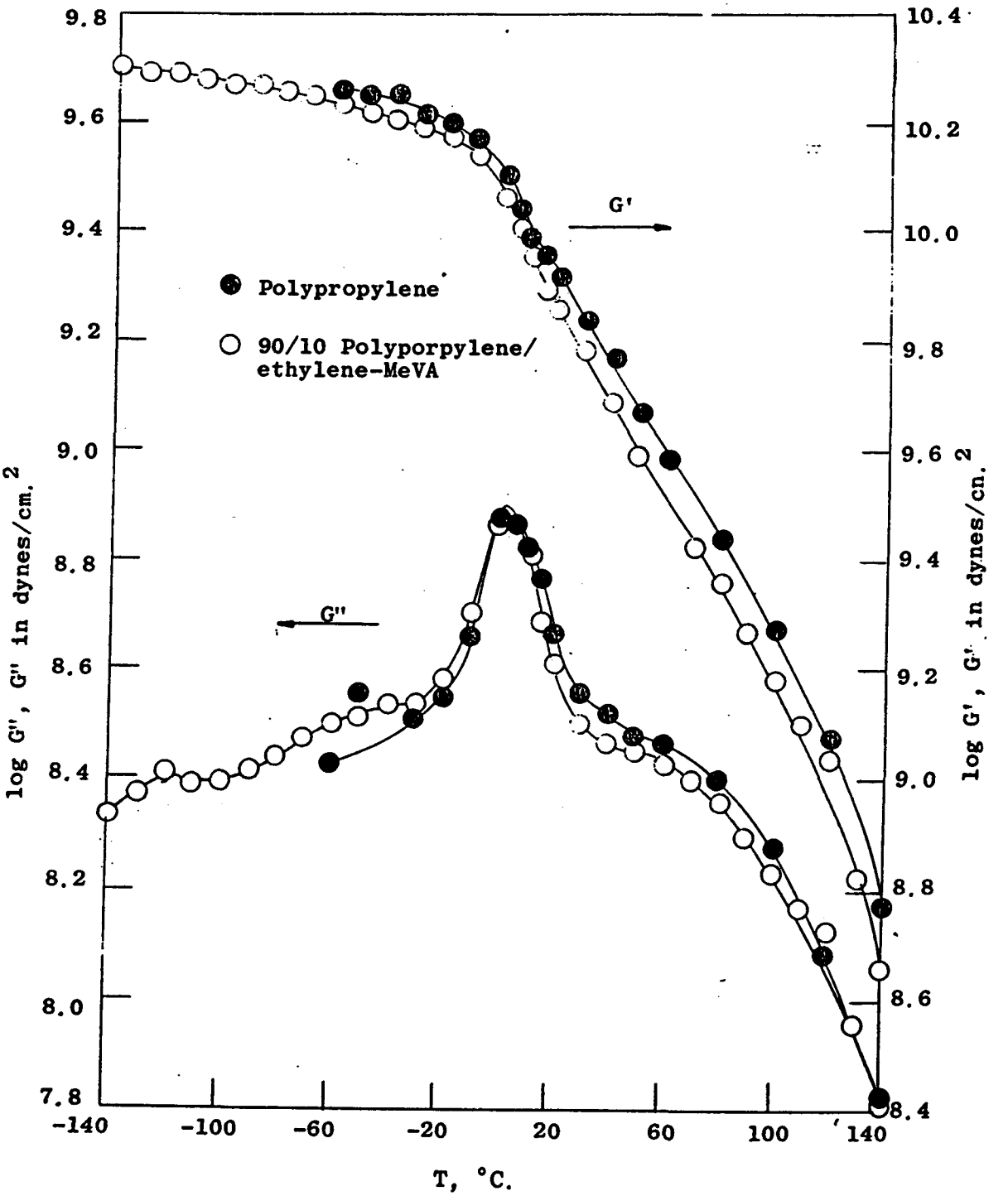
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FIGURE 4. MECHANICAL LOSS AND FREQUENCY FOR SHELL TYPE 376 POLYPROPYLENE WITH AND WITHOUT ETHYLENE-MeVA AND ETHYLENE-MeVA LOT 1433, STIRRED AUTOCLAVE, 25% MeVA.



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FIGURE 5. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS FOR SHELL TYPE 376 POLYPROPYLENE WITH AND WITHOUT THE U.C.C. DYE ASSISTANT.



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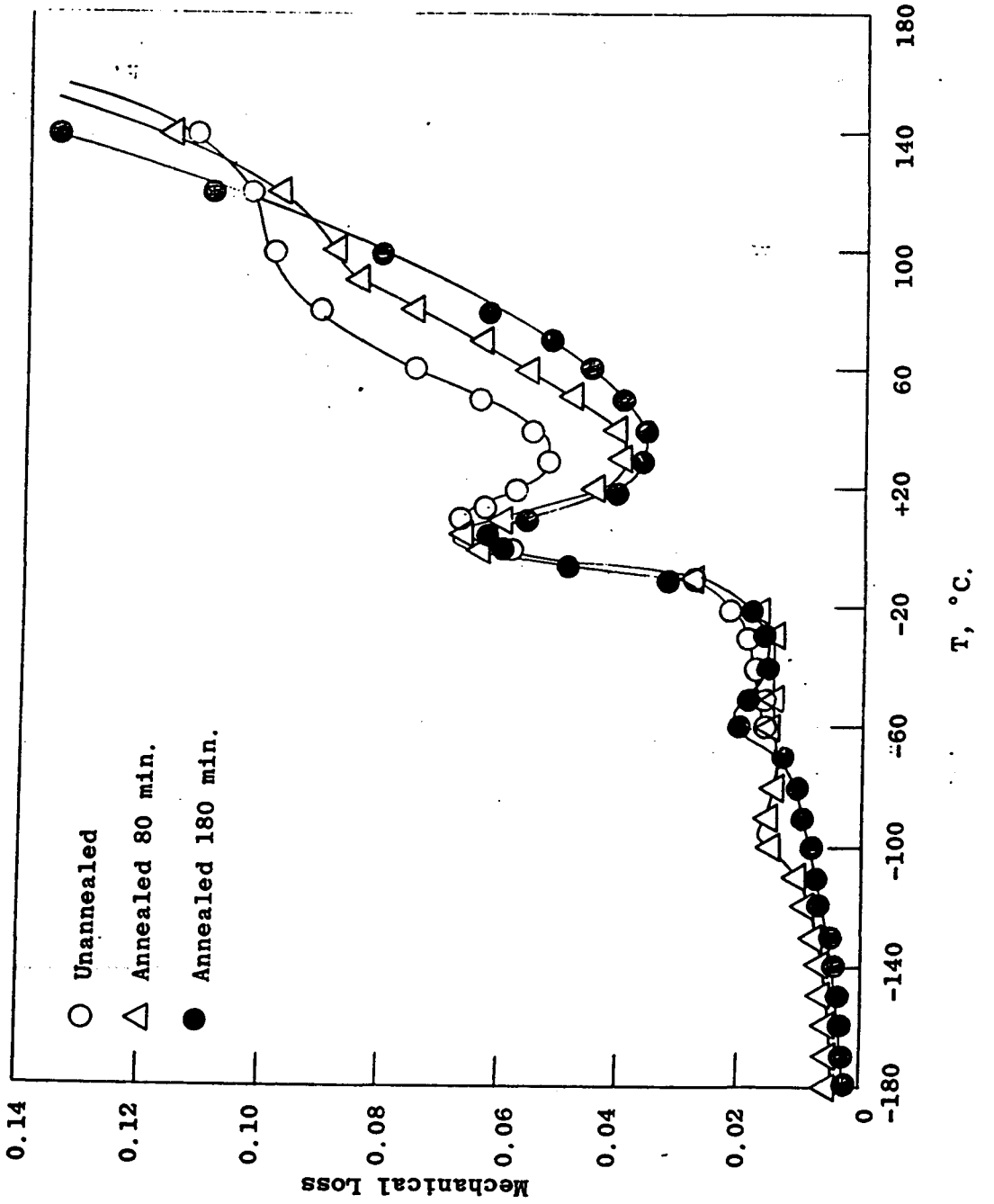


FIGURE 6. MECHANICAL LOSS FOR UNANNEALED AND ANNEALED SHELL TYPE 376 POLYPROPYLENE WITH STABILIZERS

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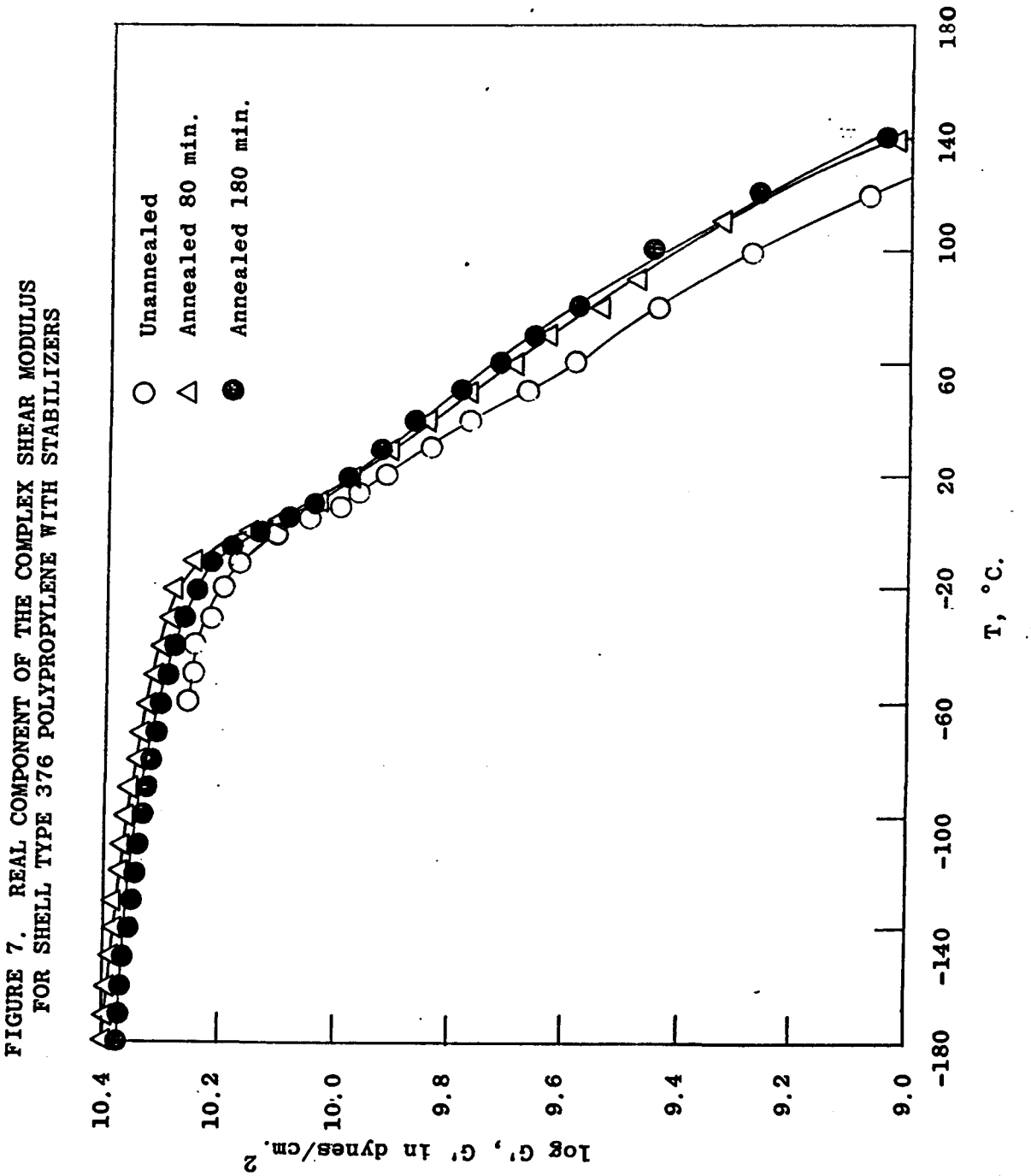
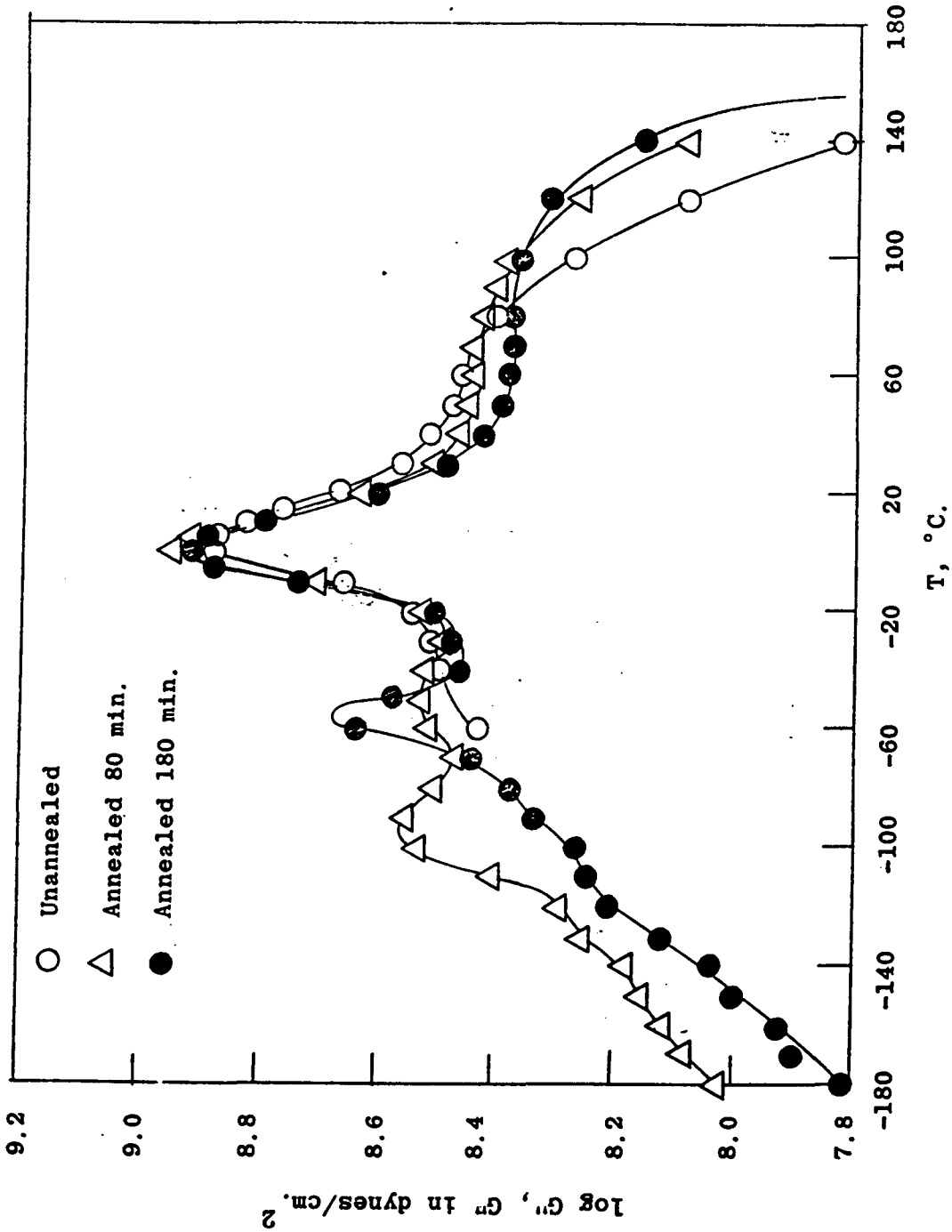


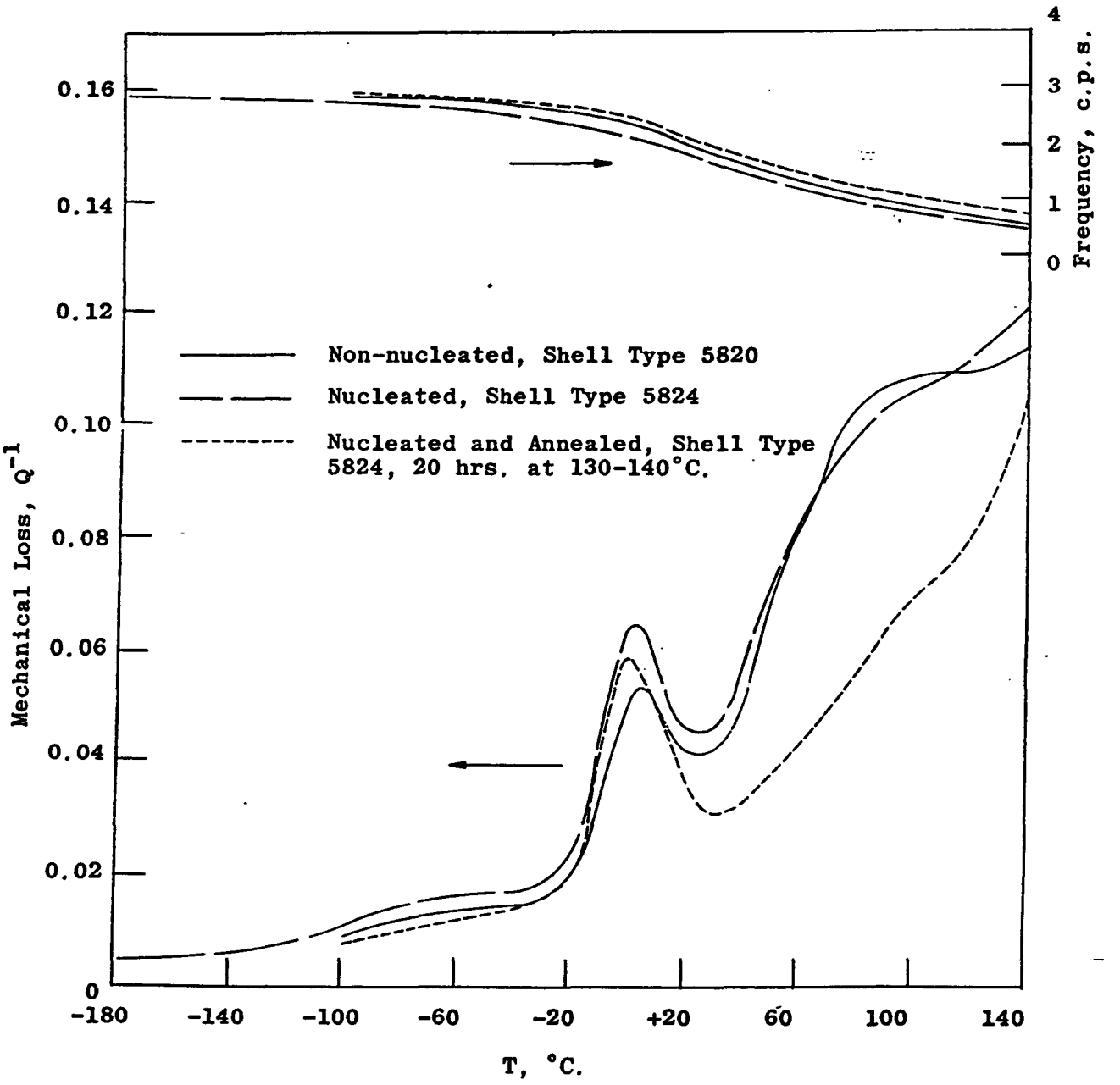
FIGURE 7. REAL COMPONENT OF THE COMPLEX SHEAR MODULUS FOR SHELL TYPE 376 POLYPROPYLENE WITH STABILIZERS

FIGURE 8. IMAGINARY COMPONENT OF THE COMPLEX SHEAR MODULUS FOR SHELL TYPE 376 POLYPROPYLENE WITH STABILIZERS.



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FIGURE 9. MECHANICAL LOSS FOR NON-NUCLEATED AND NUCLEATED POLYPROPYLENE



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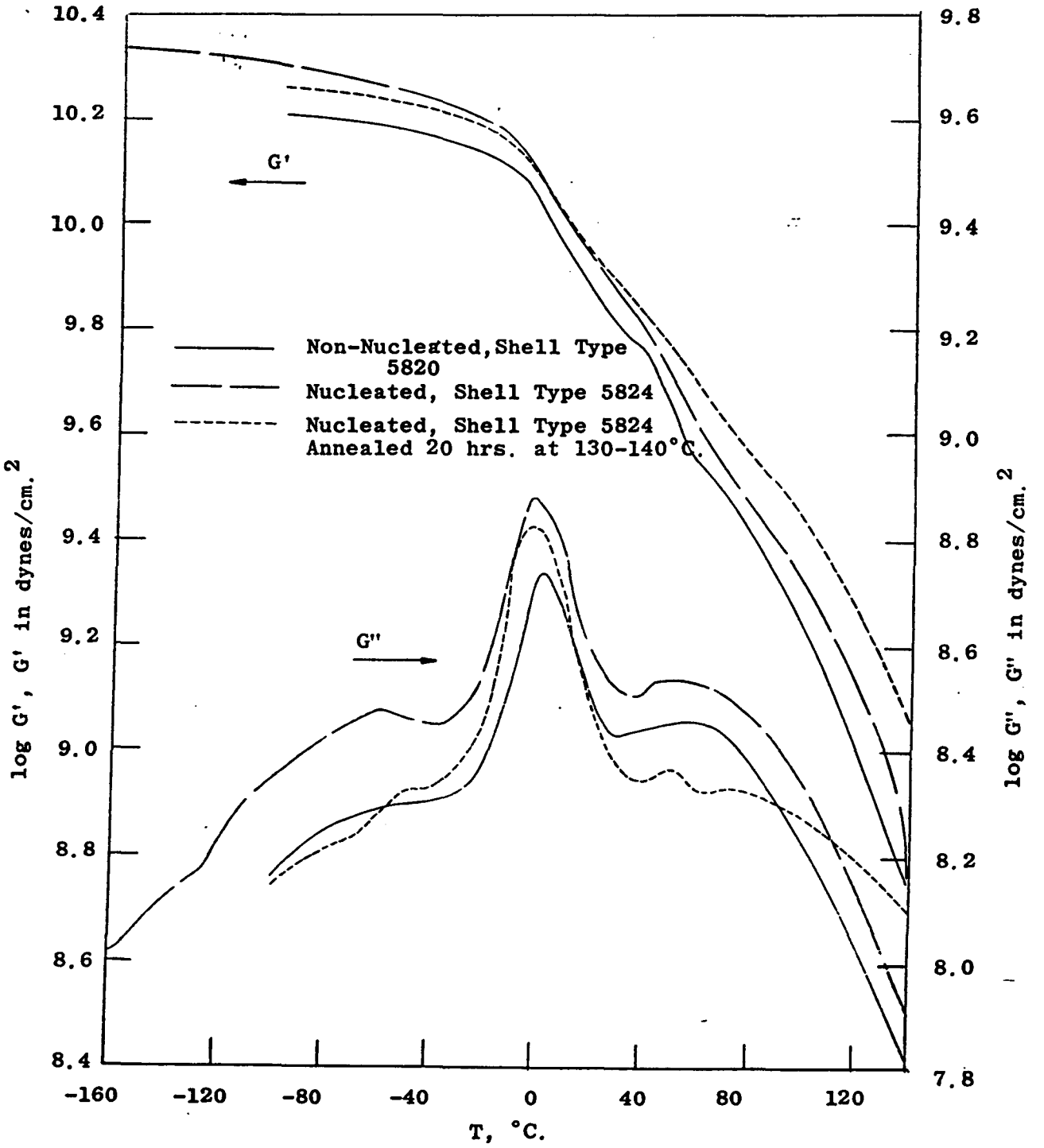


FIGURE 10. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS FOR NON-NUCLEATED AND NUCLEATED POLYPROPYLENE

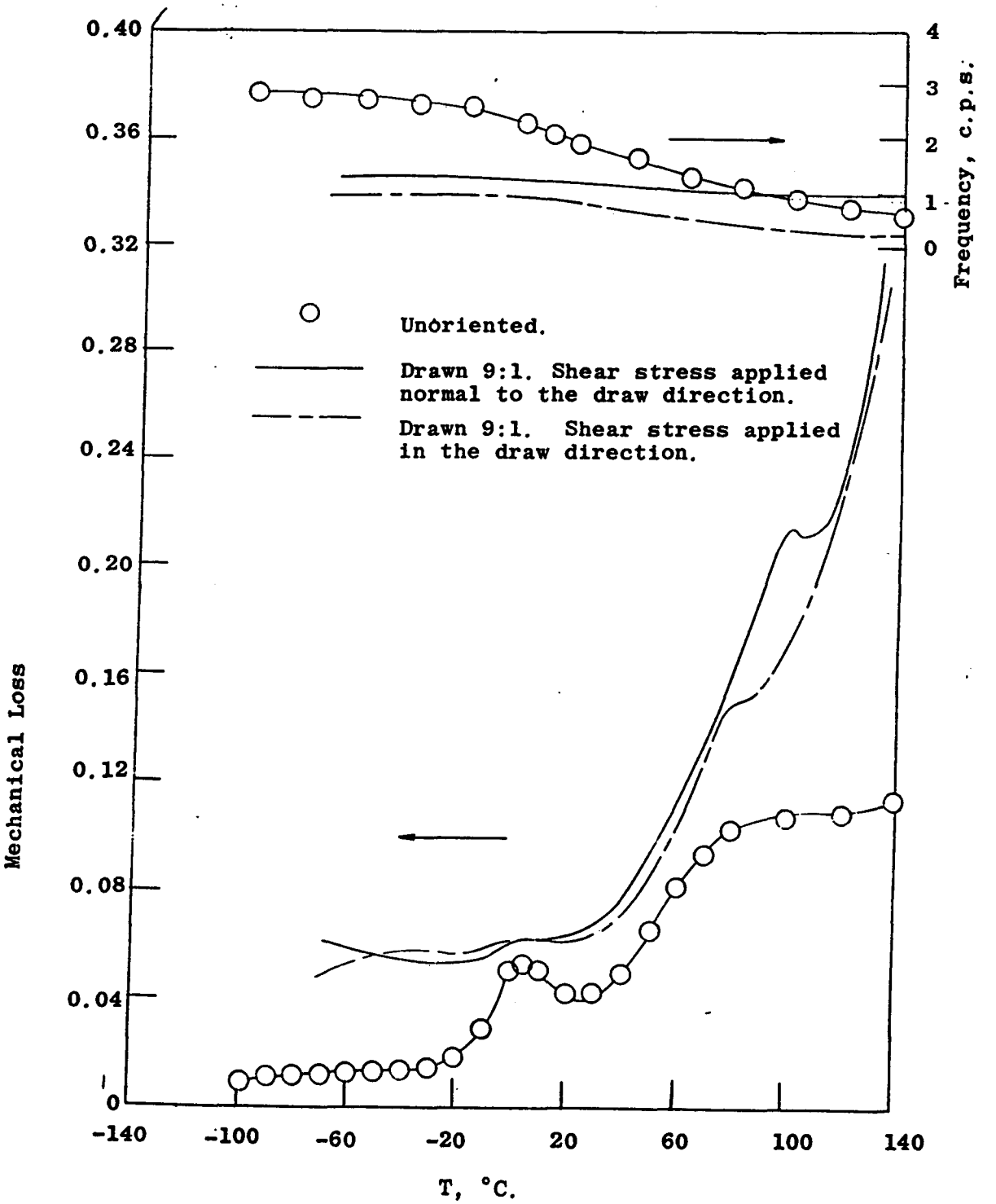


FIGURE 11. MECHANICAL LOSS AND FREQUENCY OF MEASUREMENT FOR UNORIENTED AND ORIENTED SHELL TYPE 5820 POLYPROPYLENE.

FIGURE 12. REAL COMPONENTS OF THE COMPLEX SHEAR MODULUS FOR UNORIENTED AND ORIENTED SHELL TYPE 5820 POLYPROPYLENE

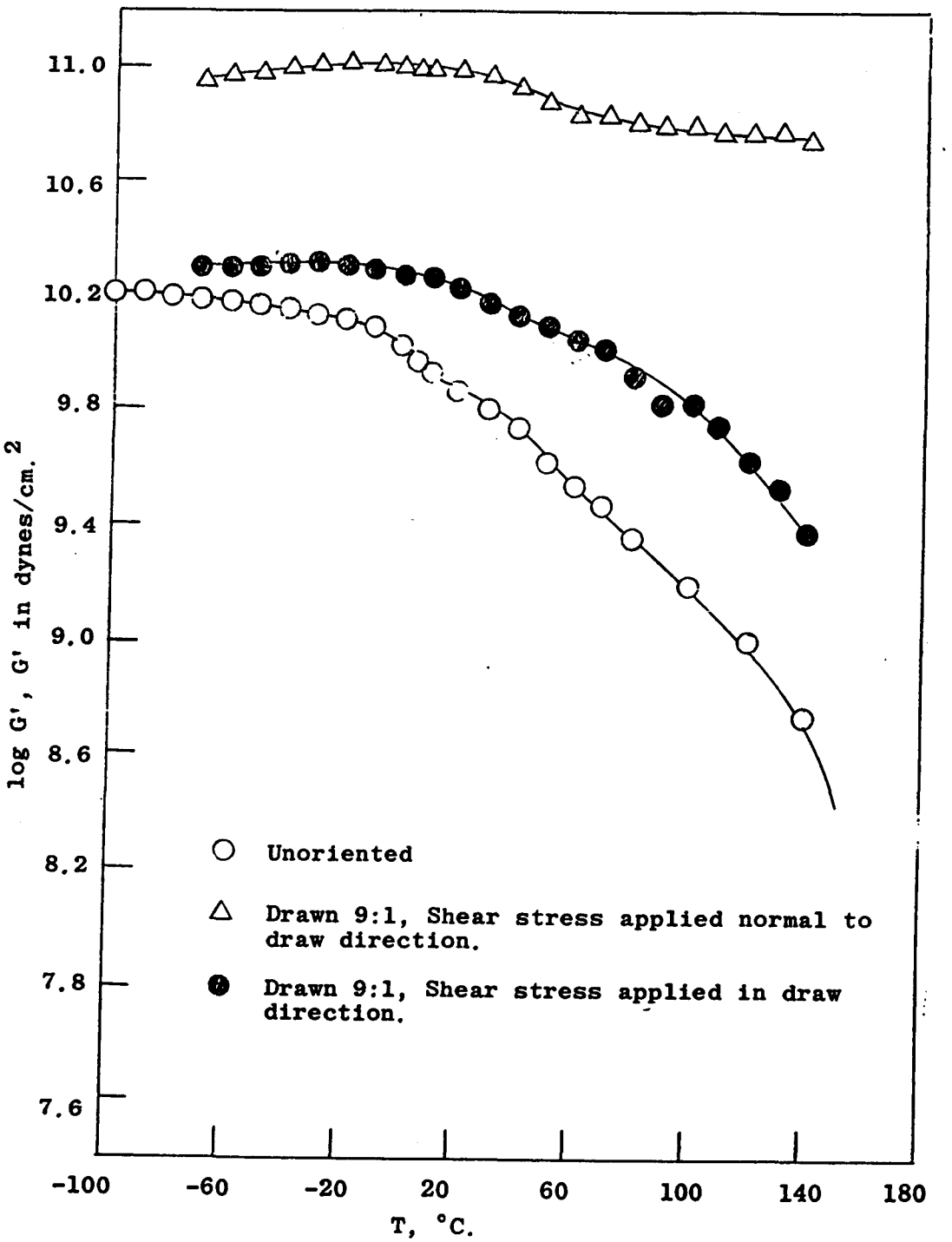
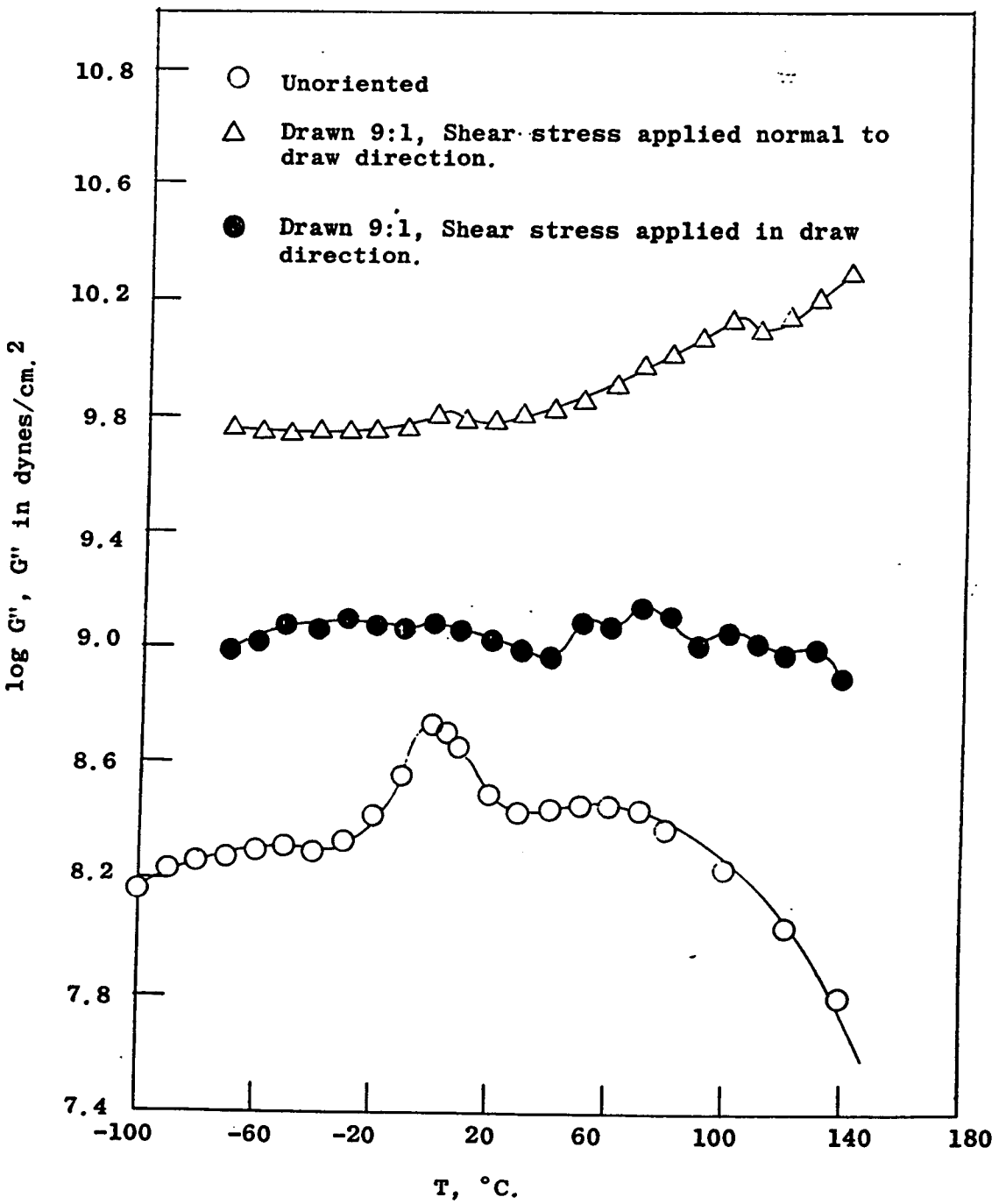
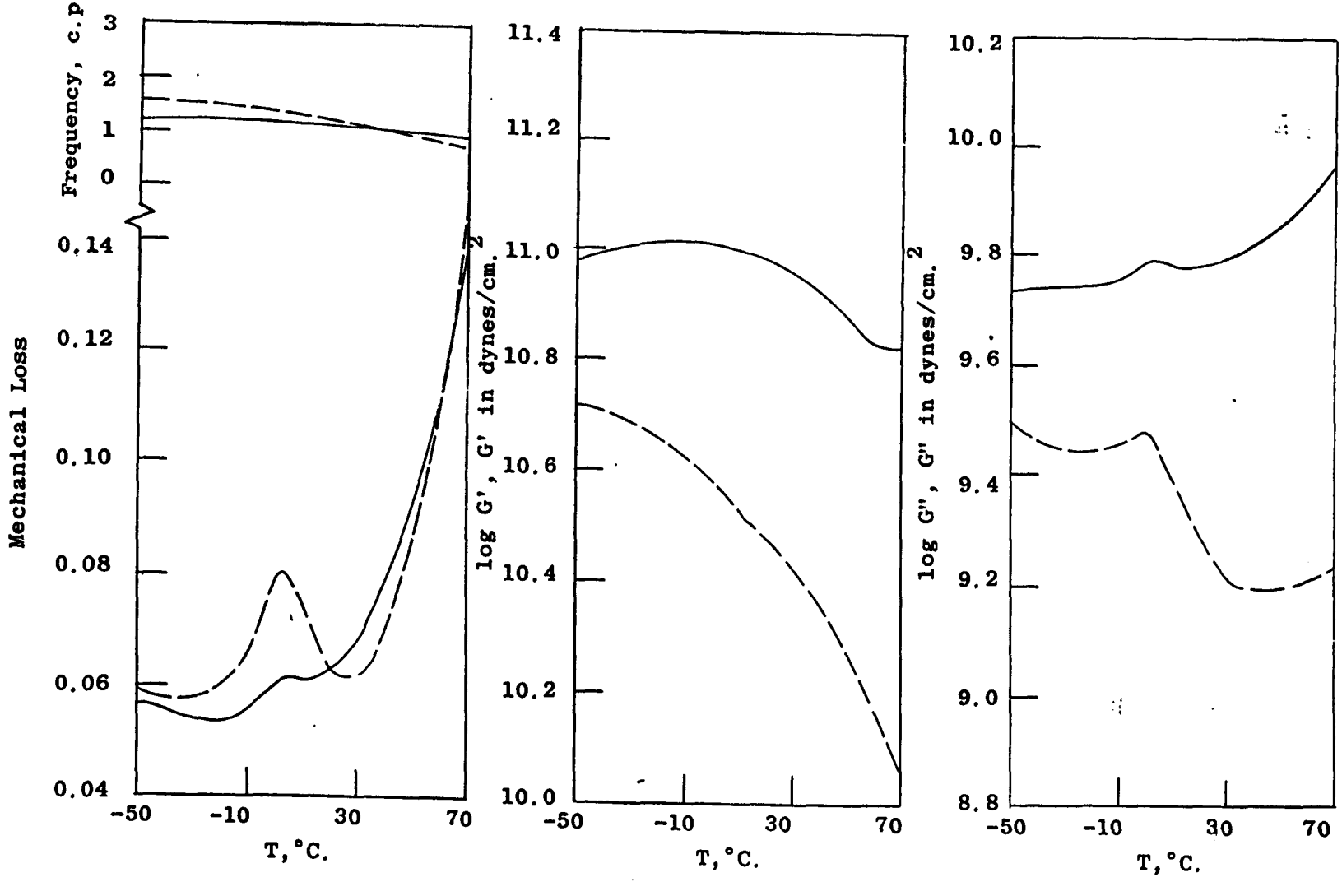


FIGURE 13. IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS FOR UNORIENTED AND ORIENTED SHELL TYPE 5820 POLYPROPYLENE



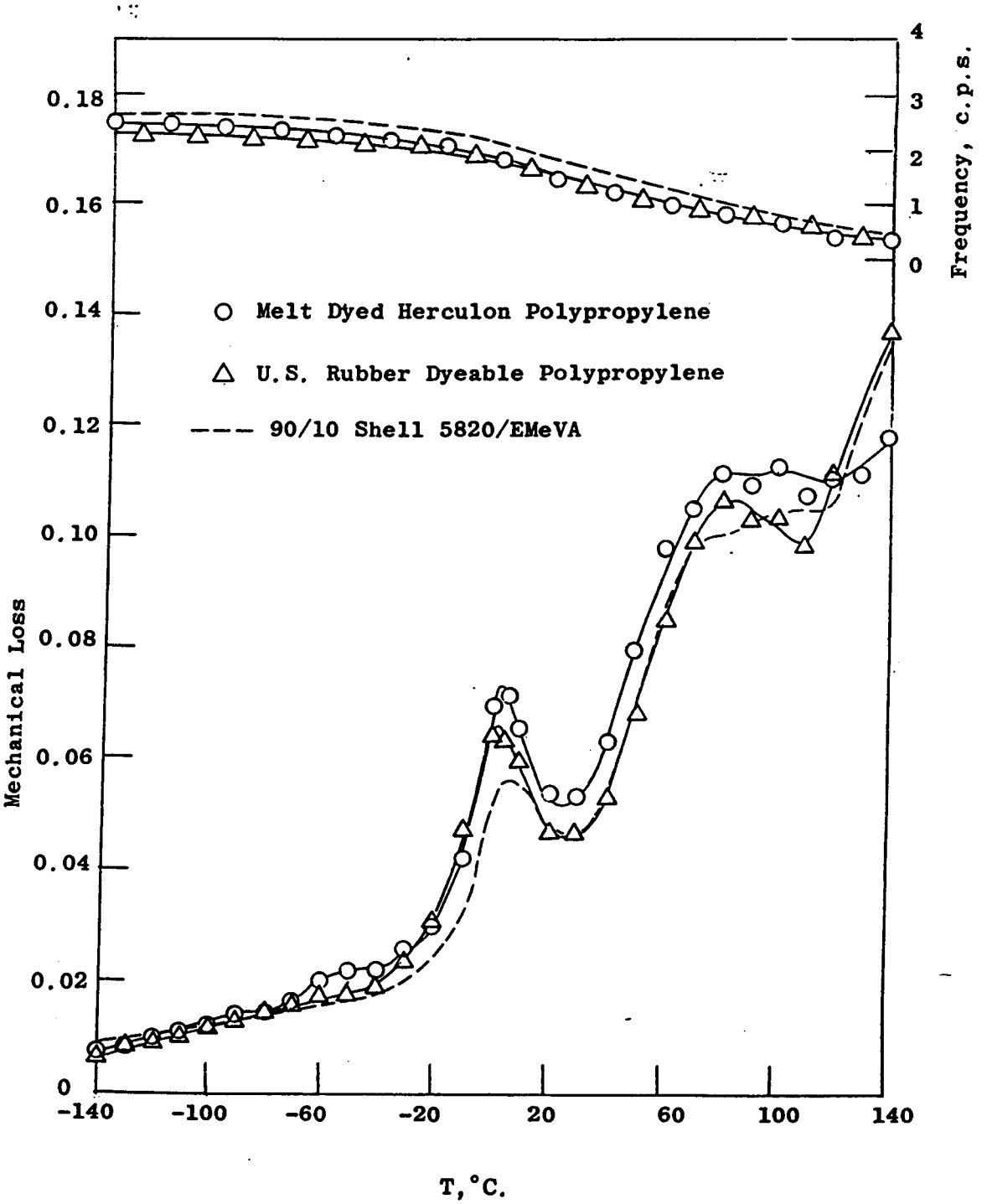
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FIGURE 14. MECHANICAL PROPERTIES FOR SHELL TYPE 5820 POLYPROPYLENE, SHEARING STRESS APPLIED NORMAL TO THE DRAW DIRECTION. —— DRAWN 9:1, — — — DRAWN 9:1 AND ANNEALED 40 MIN. AT 130-140°C.



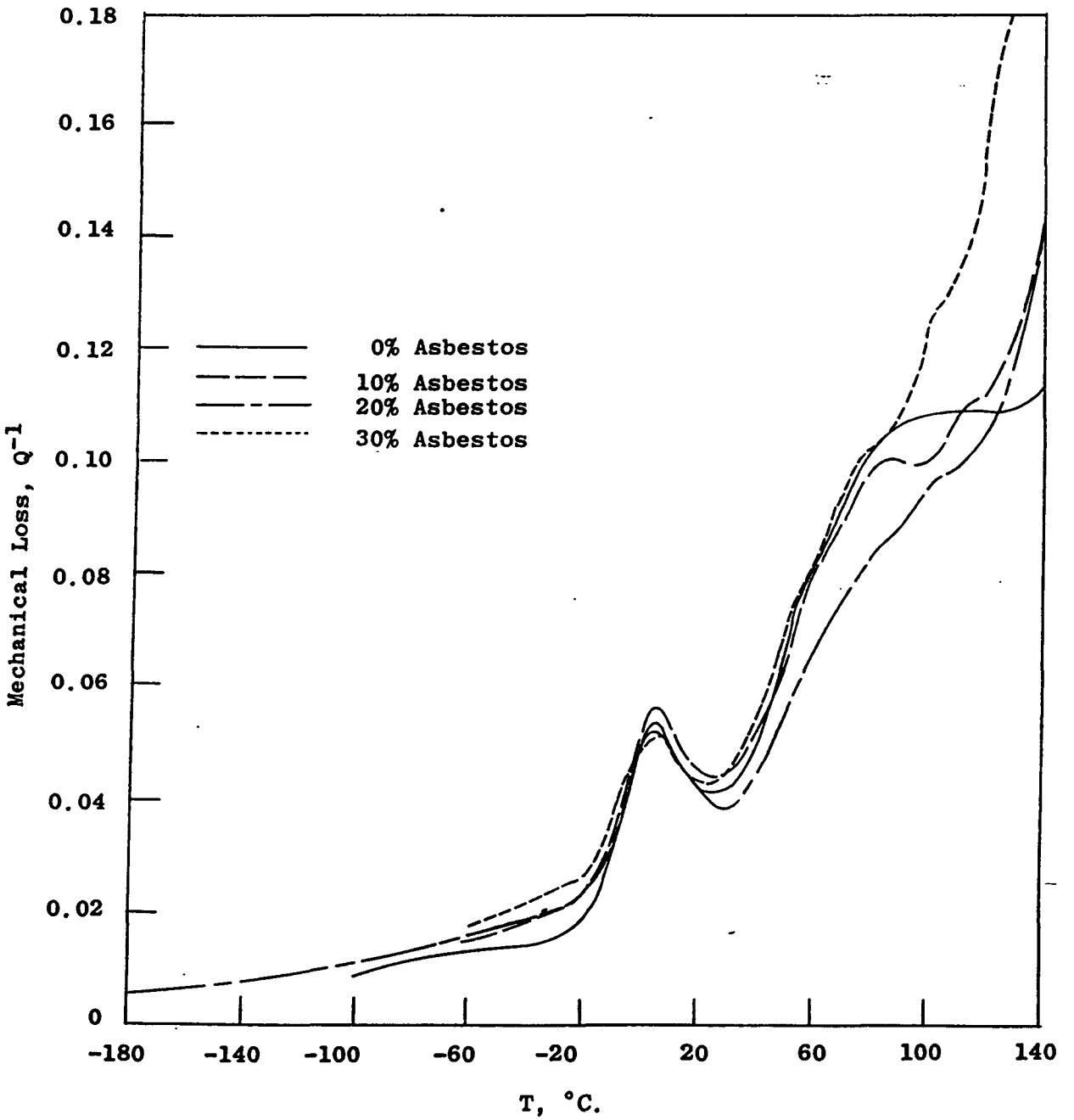
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FIGURE 15, COMPARISON OF MECHANICAL LOSS FOR COMMERCIAL DYEABLE POLYPROPYLENES



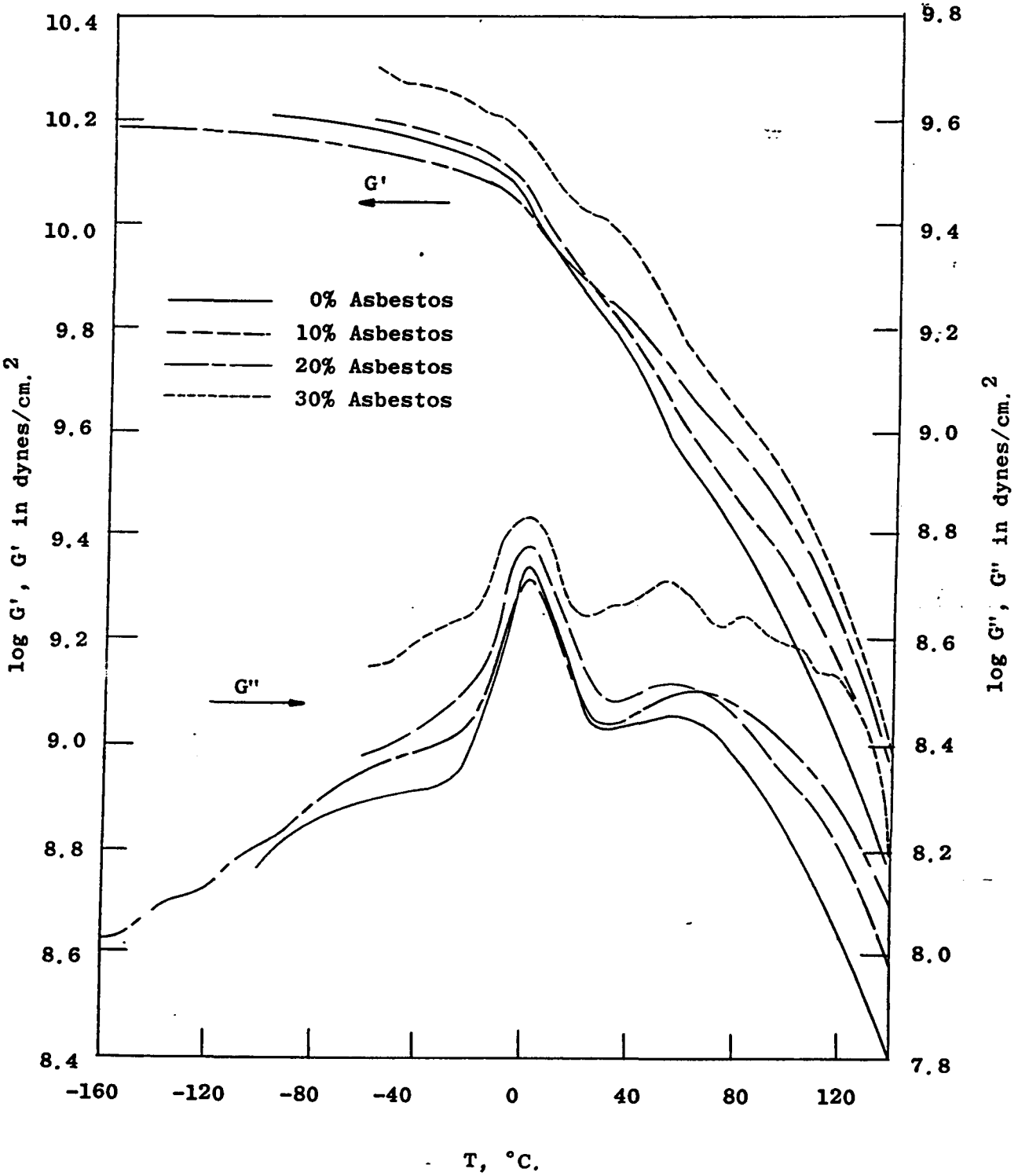
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FIGURE 16. MECHANICAL LOSS FOR SHELL TYPE 5820 POLYPROPYLENE WITH AND WITHOUT AN ASBESTOS FILLER



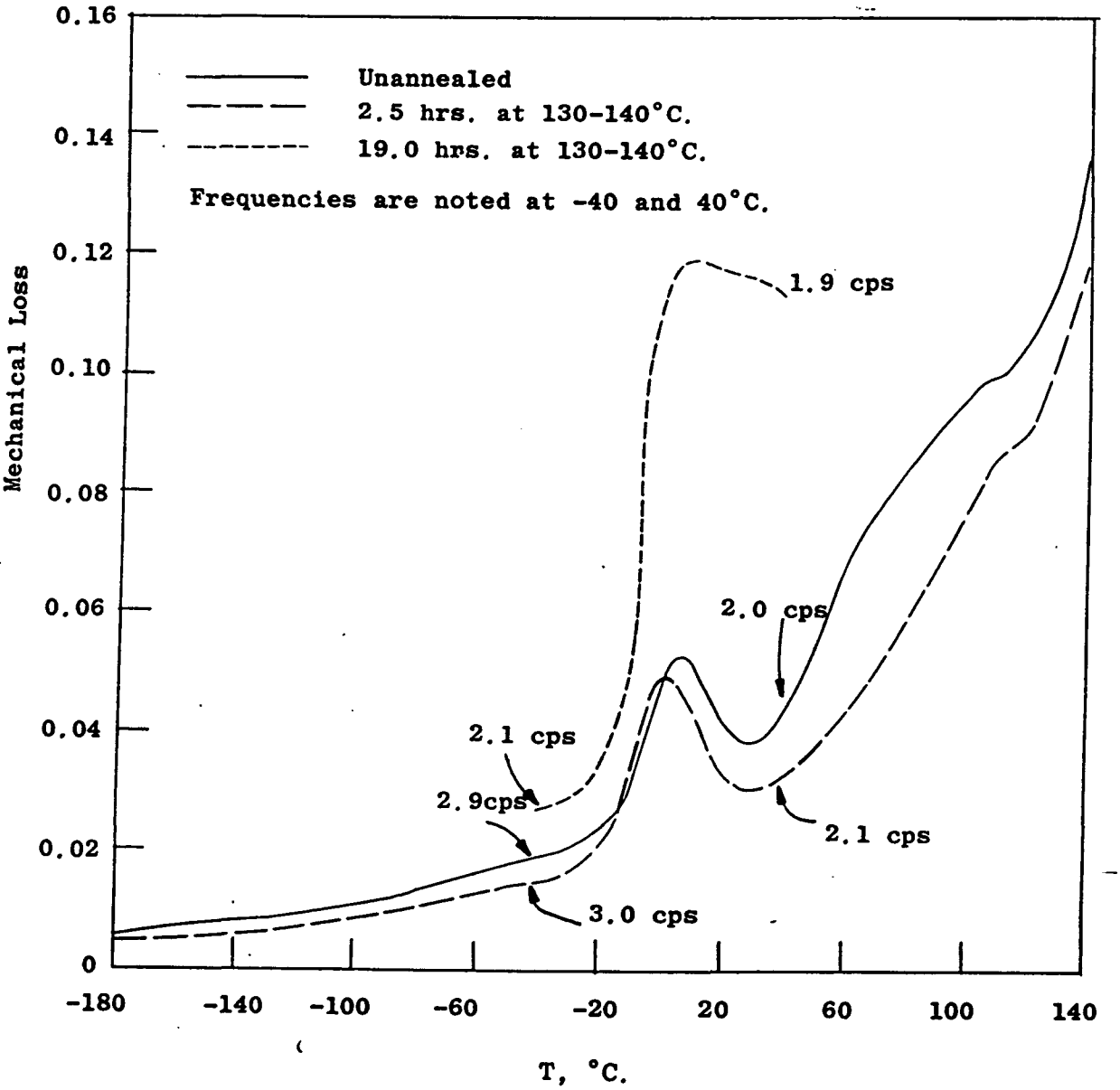
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FIGURE 17. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS OF SHELL TYPE 5820 POLYPROPYLENE WITH AND WITHOUT AN ASBESTOS FILLER



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FIGURE 18. MECHANICAL LOSS OF ANNEALED AND UNANNEALED SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS FILLER



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FIGURE 19. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS OF ANNEALED AND UNANNEALED SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS FILLER

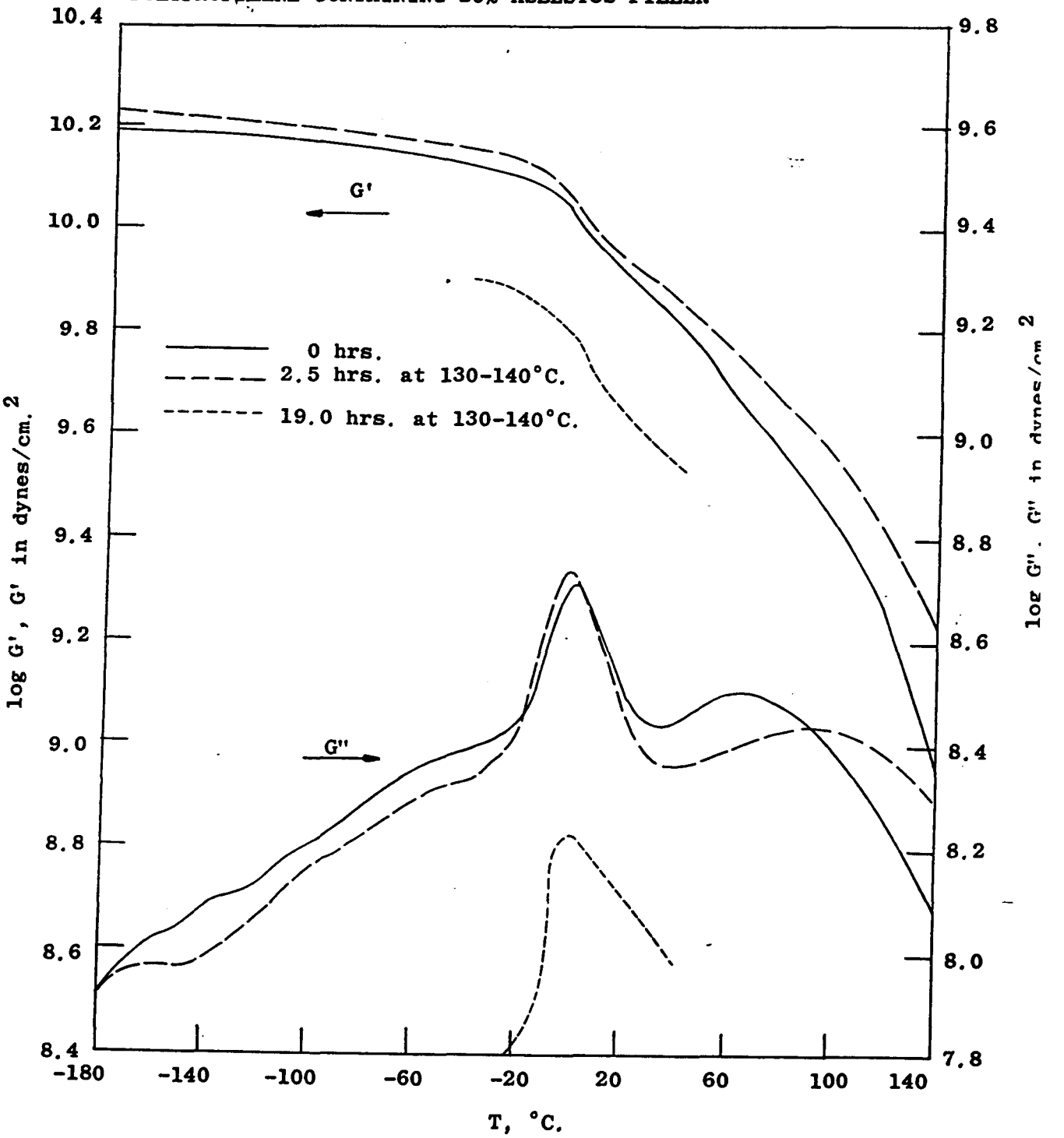
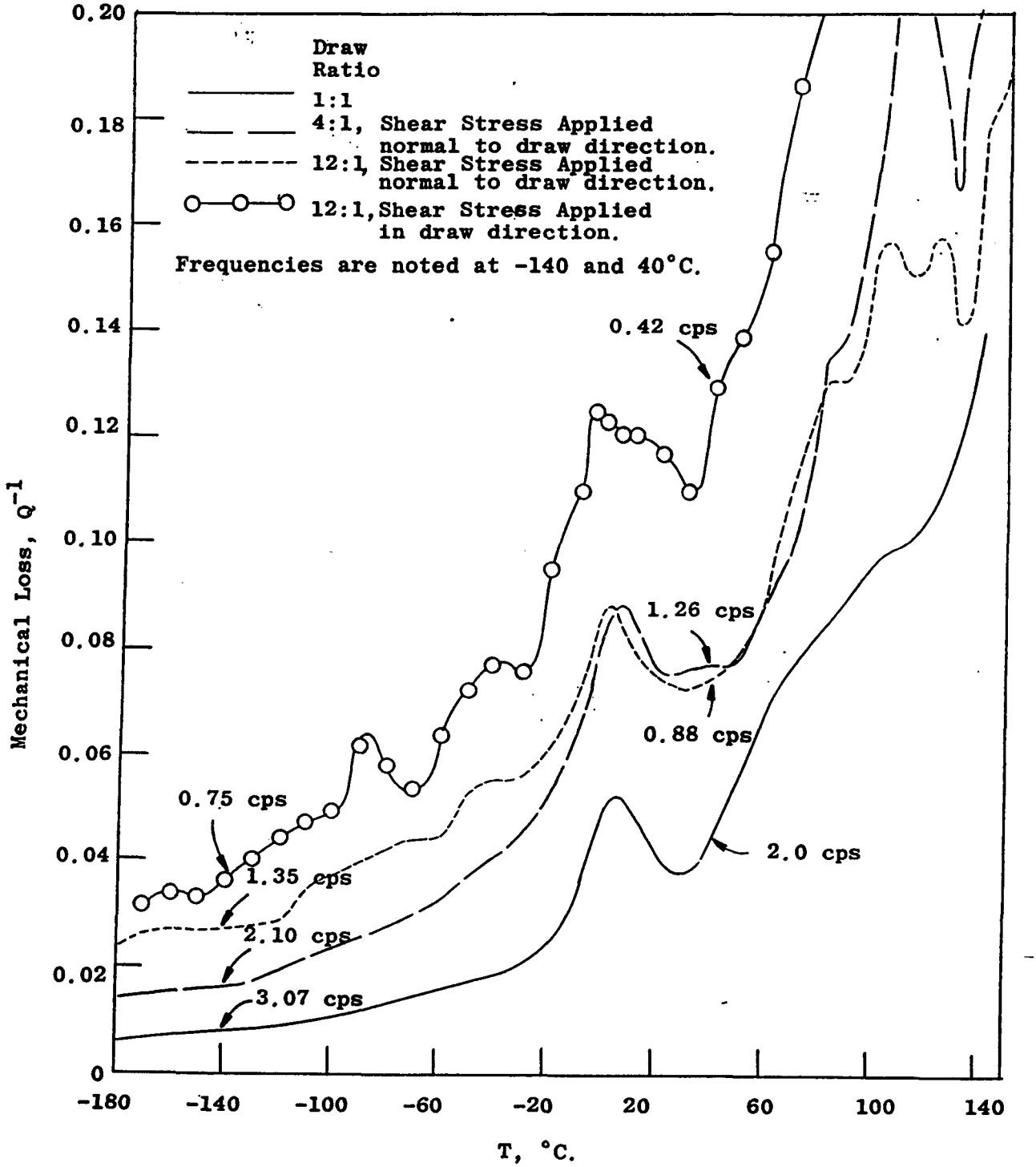
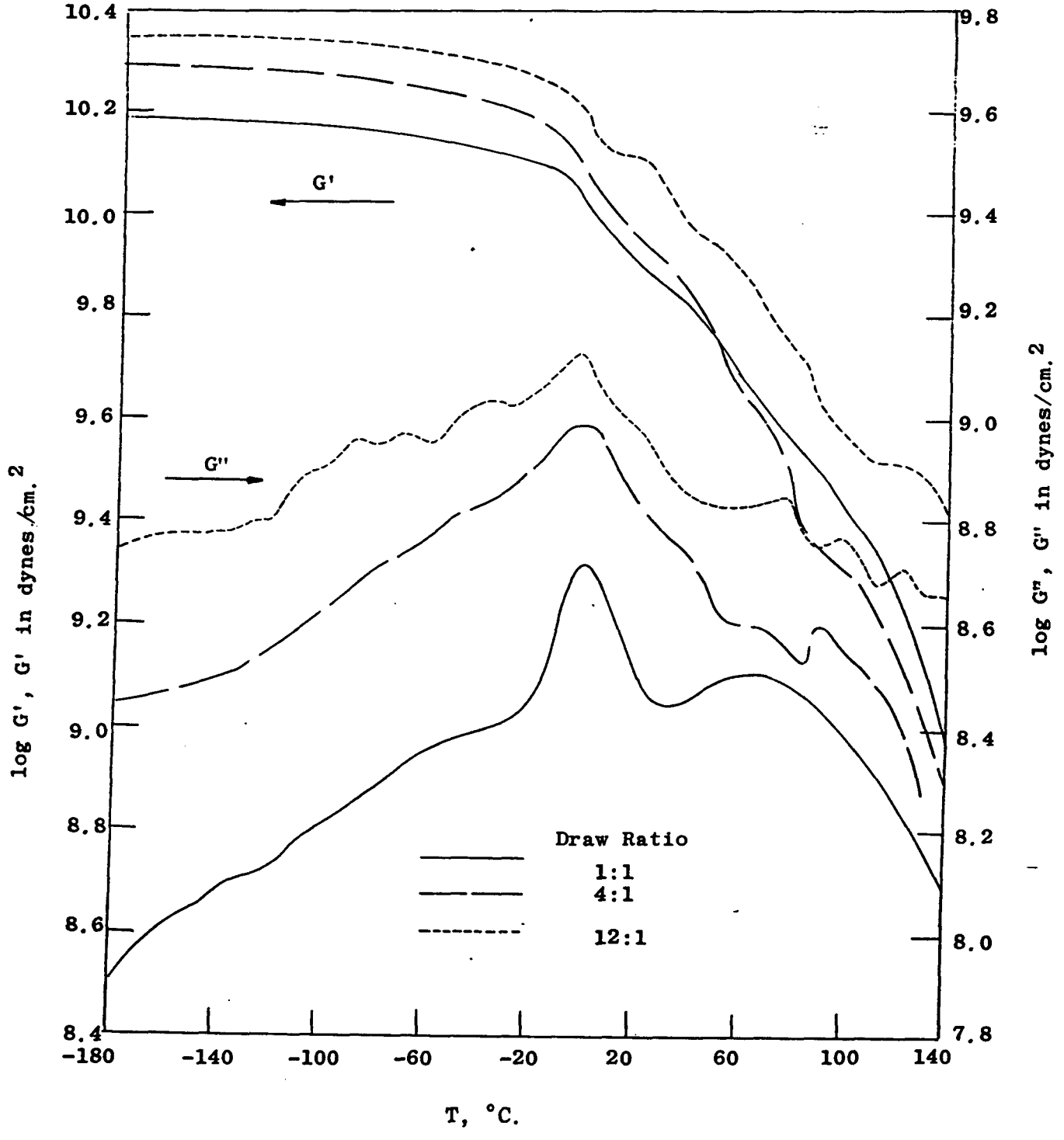


FIGURE 20. MECHANICAL LOSS FOR ORIENTED SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS



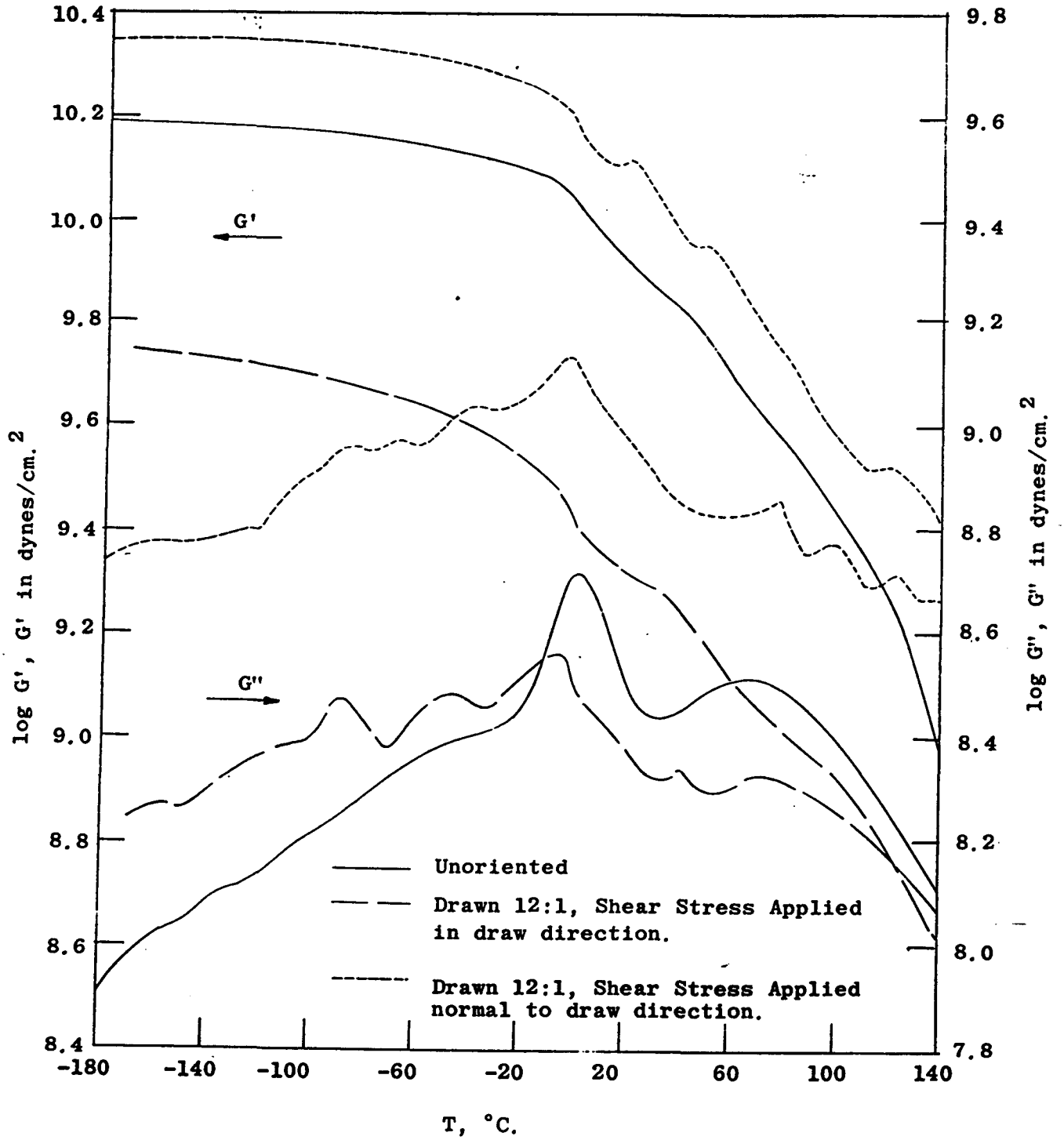
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FIGURE 21. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS OF ORIENTED SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS. SHEAR STRESS APPLIED NORMAL TO DRAW DIRECTION FOR ORIENTED SPECIMENS.



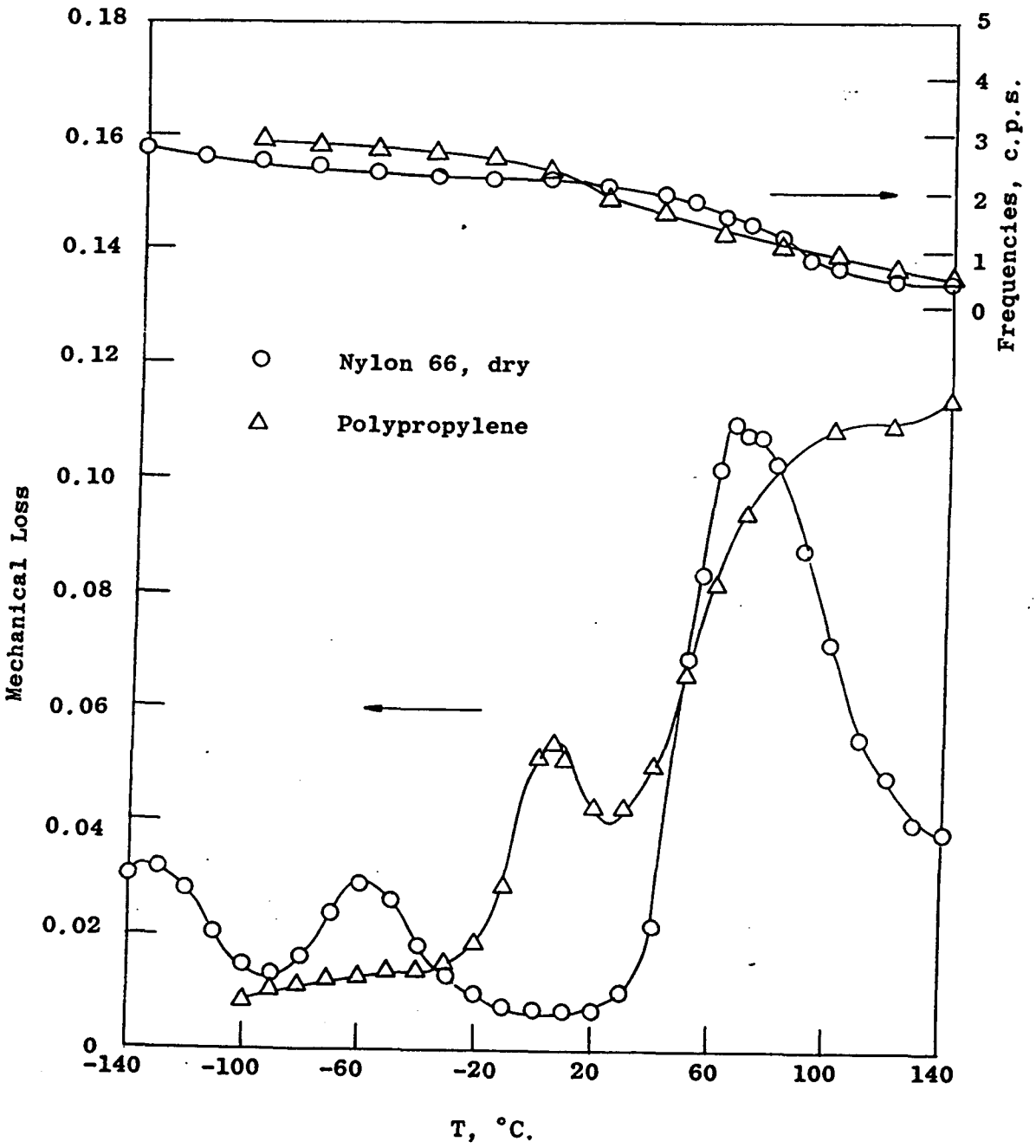
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FIGURE 22. REAL AND IMAGINARY COMPONENTS OF THE COMPLEX SHEAR MODULUS IN AND NORMAL TO DRAW DIRECTION FOR SHELL TYPE 5820 POLYPROPYLENE CONTAINING 20% ASBESTOS



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FIGURE 23. COMPARISON OF MECHANICAL LOSS FOR SHELL TYPE 5820 POLYPROPYLENE AND DRIED ZYTEL 101 (NYLON 66). THE NYLON WAS DRIED FOR 48 HOURS IN A DESICCATOR OVER $CaSO_4$.



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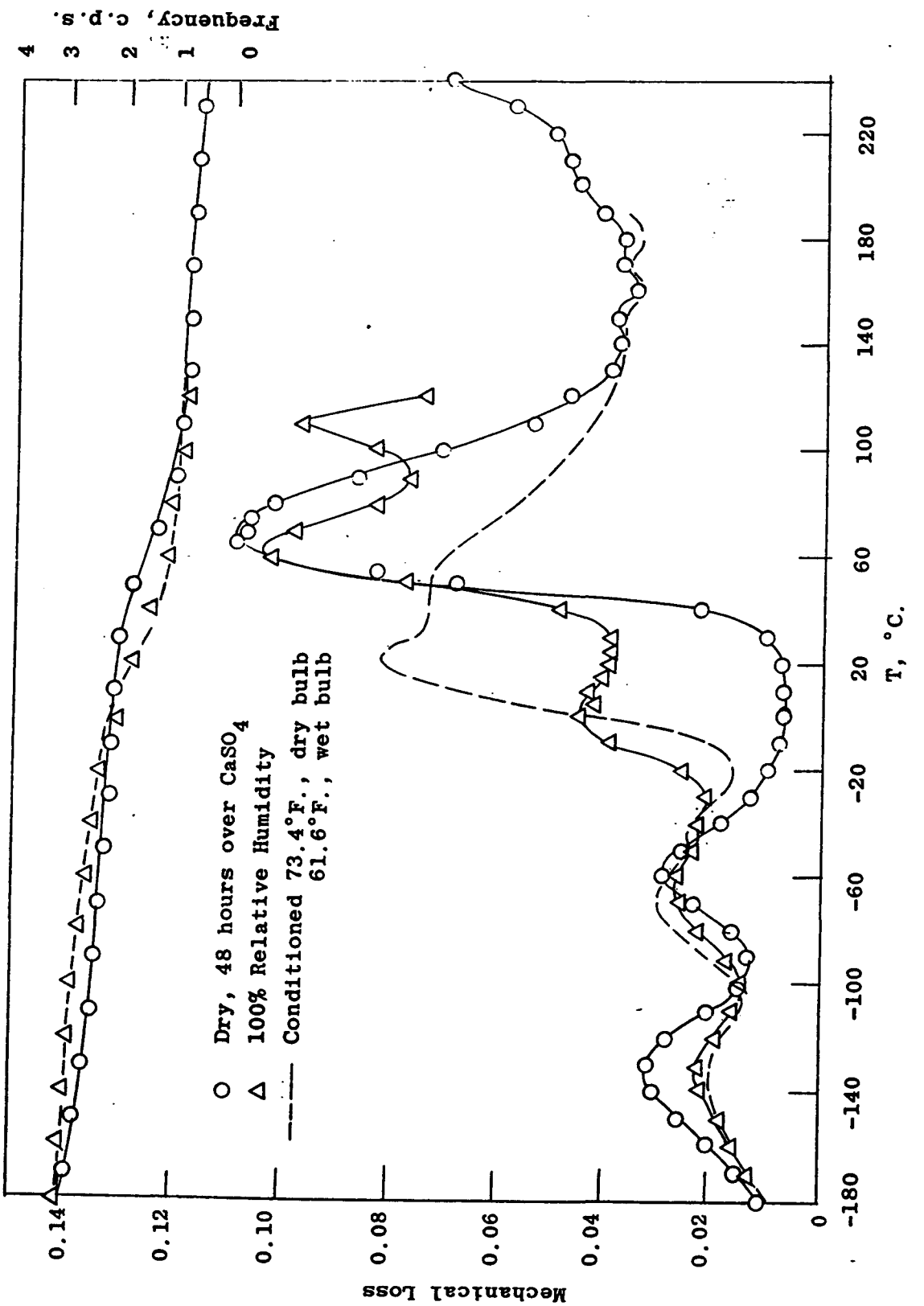


FIGURE 24. MECHANICAL LOSS FOR ZYTEL 101 (NYLON 66) AT VARIOUS HUMIDITIES

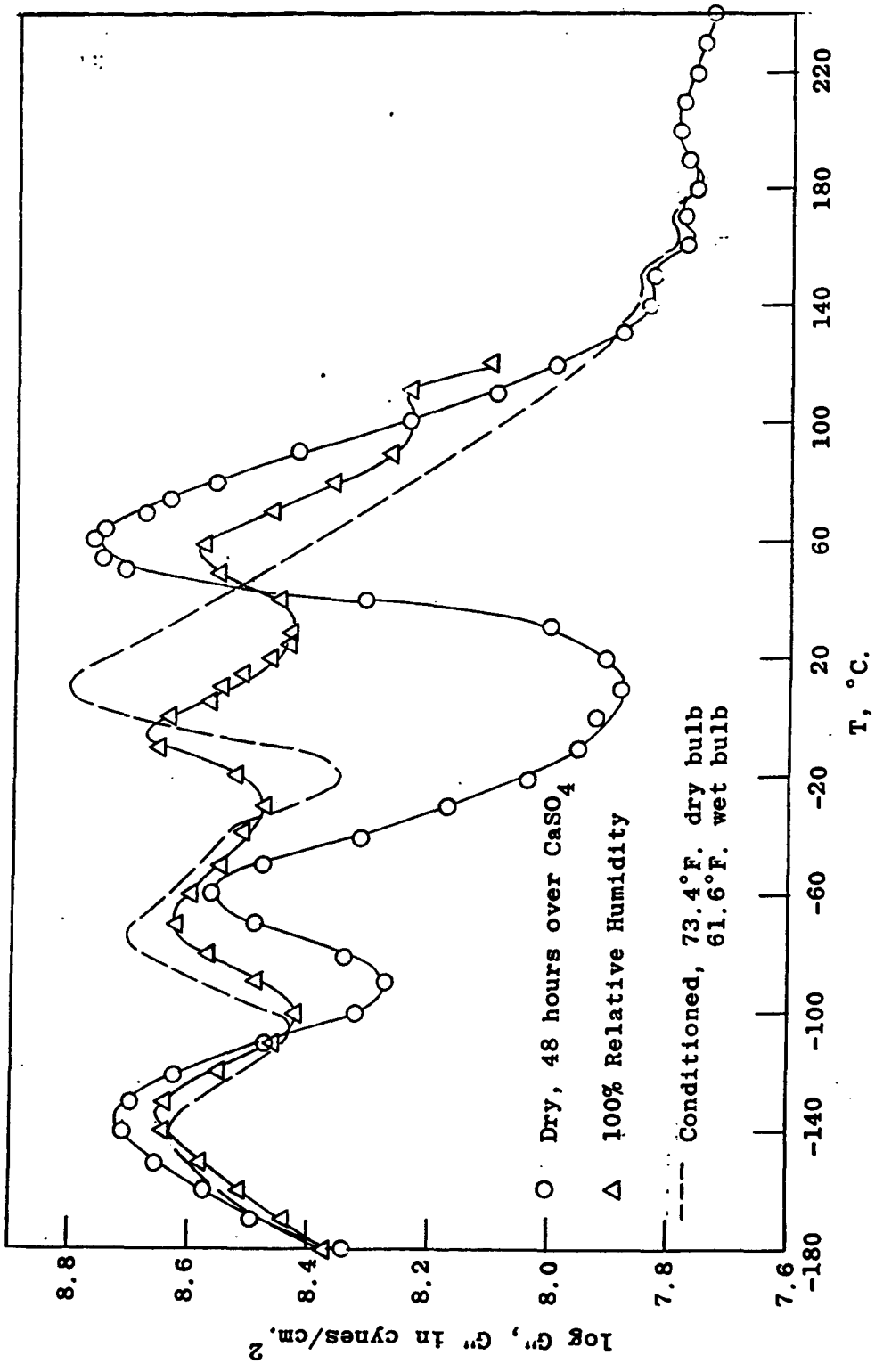
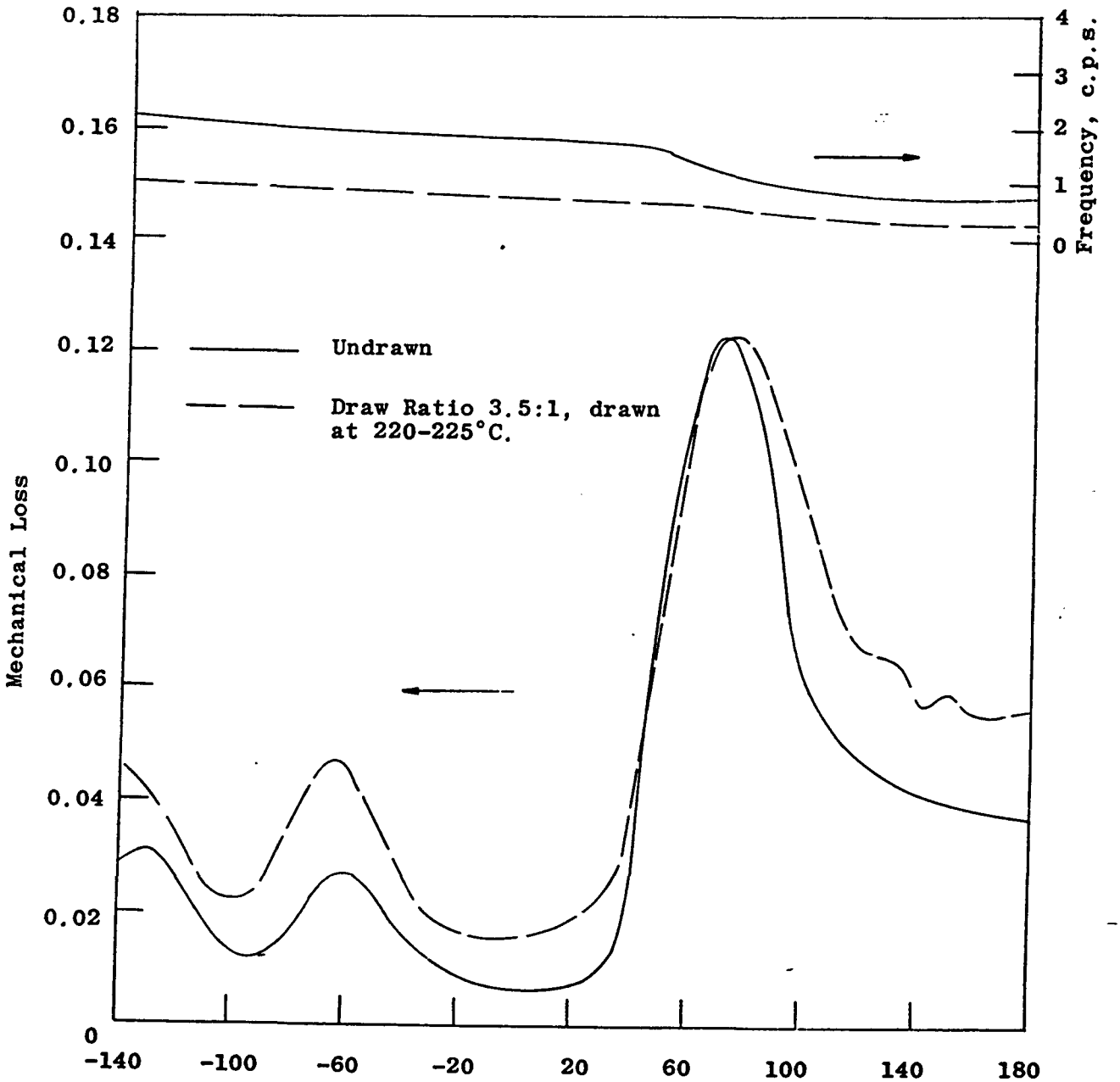


FIGURE 25. IMAGINARY COMPONENT OF COMPLEX SHEAR MODULUS FOR ZYTEL 101 (NYLON 66) AT VARIOUS HUMIDITIES

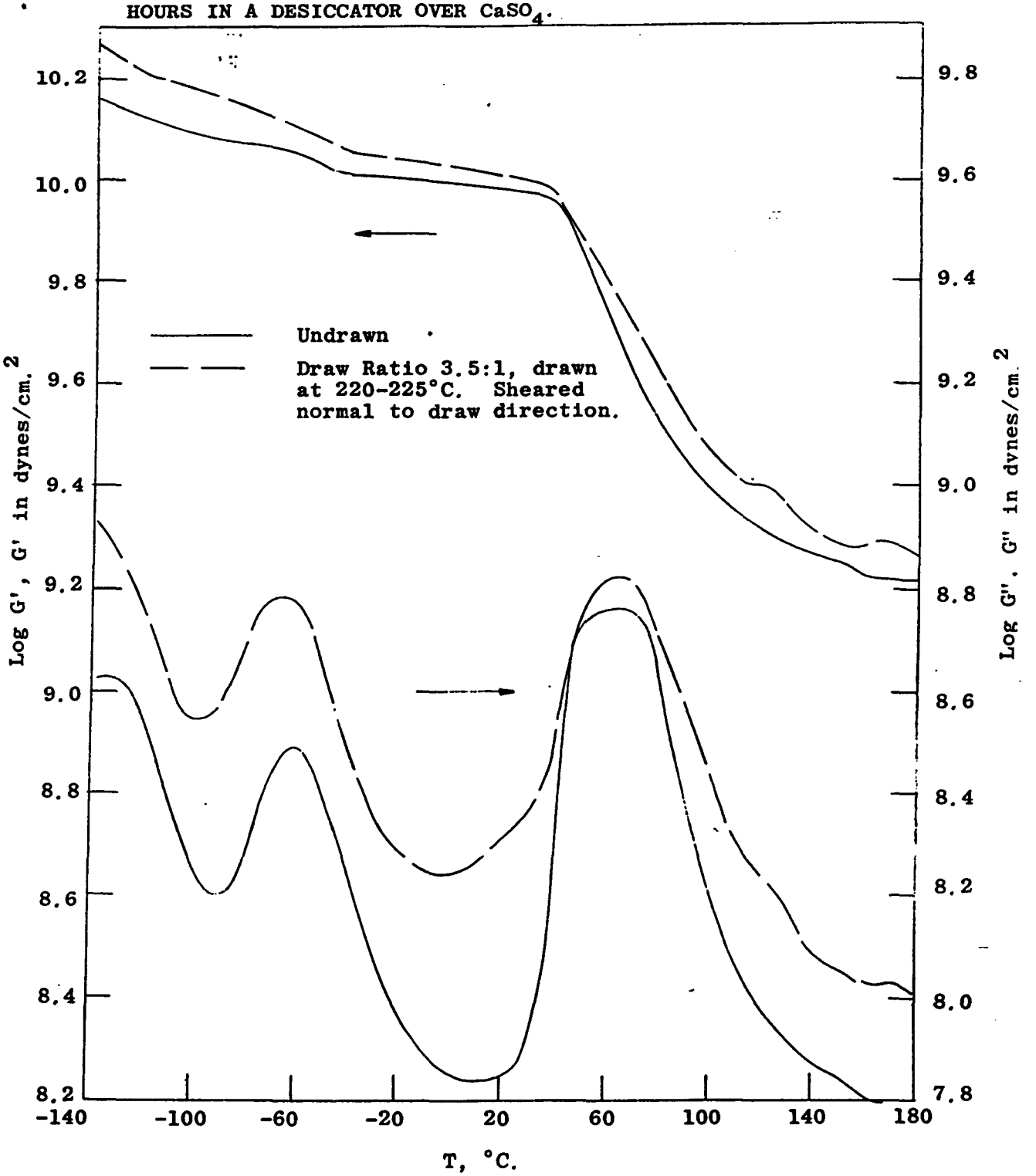
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FIGURE 26. EFFECT OF ORIENTATION ON MOLDED NYLON 501 YARN (NYLON 66). DRIED FOR 48 HOURS IN A DESICCATOR OVER $CaSO_4$. DRAWN SPECIMEN WAS SHEARED NORMAL TO THE ORIENTATION DIRECTION.



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FIGURE 27. EFFECT OF ORIENTATION ON THE COMPONENTS OF THE COMPLEX SHEAR MODULUS OF MOLDED NYLON 501 YARN (NYLON 66). DRIED 48 HOURS IN A DESICCATOR OVER $CaSO_4$.



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