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THE COLLEGE OF WILLIAM AND MARY IN VIRGINIA
WILLIAMSBURG 23185

DEPARTMENT OF CHEMISTRY
(804) 253-4664

July 9, 1985

Mr. Howard J. Osborn
Patent Counsel
NASA Langley Research Center
Mail Stop 279
Hampton, VA 23665

Dear Mr. Osborn,

This is to notify you that the patent for which the inventor through the contractor, elected to retain title to (in correspondence dated November 26, 1984) under grant NAG 1-237, has been filed with the United States Patent Office. The patent application is dated May 1, 1985 and bears serial number 729,459.

Sincerely,

David Kranbuehl

David Kranbuehl
Professor of Chemistry

(NASA-CR-176256) CHARACTERIZATION OF THE RELATIONSHIP OF THE CURE CYCLE CHEMISTRY TO CURE CYCLE PROCESSING PROPERTIES Report, period ending 31 Jul. 1985 (College of William and Mary) 33 p HC A03/MF A01 N86-11339

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DAA/Langley

THE COLLEGE OF WILLIAM AND MARY

Department of Chemistry

Williamsburg, Virginia 23185

Report for Period Ending July 31, 1985

NASA Research Grant Number NAG 1-237

Entitled

Characterization of the Relationship of the Cure Cycle Chemistry to Cure Cycle Processing Properties

David Kranbuehl 8/23/85

David E. Kranbuehl Date
Principal Investigator
(804)-253-4563

Progress continues to be made toward achieving our long-range goals of relating dielectric measurements to the chemistry and physics of the cure cycle process and using on-line dielectric instrumentation for closed loop cure cycle control. Measurements are made over a frequency range of six decades and a temperature range of from 20° to 380°C. The complex permittivity (ε^*) is calculated from measurements of C & G. This is an intensive property which is characteristic of the state of cure of the material itself and not dependent upon sample geometry.

From its frequency dependence, the complex permittivity can be separated into ionic and dipolar components. In the frequency range where ionic contributions dominate the dielectric signal, the relative ease of ionic mobility through the resin medium can be determined. This is both a function of the resin's viscosity and the temperature of measurement. In the region where the imaginary part of the complex permittivity, ε'', is proportional to f^{-1}, an apparent specific conductivity σ_{app} can be calculated. This quantity has been directly related to the viscosity of the system. In regions where the total ionic contribution is due to d.c. conductivity, subtracting σ from ε'' gives the dipolar loss. The frequency dependence of this term is also a function of viscosity.

Previous work concentrated on understanding both the chemistry and dielectric signals of the NASA formulated polyimides LaRC-160 and PMR-15 and a thermoplastic polysulfone. Recent work has extended our data base to epoxy resins.

The team effort with other members of the NASA community has continued. We have published several papers on the EPON system with joint authorship. We are currently investigating a system developed in-house at NASA-Langley:

polylarylene ether (PAE).

Substantial effort during this past year has gone into implementing a Perkin-Elmer DSC and creating software to interpret the data. DSC results along with viscosity and chemical characterization data will be correlated with DDA. An FTIR capability is also under development.

The accompanying paper delivered at the May 1985 SPE meeting describes in greater detail several aspects of current completed work.

Talks and posters have been presented at the following conferences:

Gordon Research Conference on Dielectric Phenomena, Holderness Academy 1984

Twelfth Biennial Polymer Symposium, Maui, Hawaii, Dec. 1984

30th SAMPE Symp., Anaheim, California, March 1985

43rd Annual Tech. Conference, Society of Plastics Engineers, Washington, D.C., April 1985

Conference on Review of Progress in Quantitative Nondestructive Evaluation, Williamsburg, Virginia, June 1985

ACS Workshop on Polyimides, Reno, Nevada, June 1985

The following articles have been prepared:

In Print

D. E. Kranbuehl, S. E. Delos, E. C. Yi, J. T. Mayer, T. Hou and W. Winfree, SAMPE Symp. Ser., 30, 638 (1985).

D. E. Kranbuehl, S. E. Delos, E. C. Y, J. T. Mayer, T. Hou and W. Winfree, Conf. Proc. of the Society of Plastics Engineers, 43, 311 (1985)

D. E. Kranbuehl, S. E. Delos, E. C. Yi, M. S. Hoff and M. E. Whitham, Proc. of the ACS Div. of Polymeric Materials: Science and Engineering 53, 191 (1985)

In Press

D. E. Kranbuehl, S. E. Delos, E. C. Yi and J. T. Mayer, Proceedings of Progress in Quantitative NDE, in press.

D. E. Kranbuehl, S. E. Delos, and P. K. Jue, Polymer, in press.

D. E. Kranbuehl, "Electrical Methods for Cure Monitoring," Developments In Reinforced Plastics, Elsevier Science publishers, LTD., in press.

DYNAMIC DIELECTRIC ANALYSIS: NONDESTRUCTIVE MATERIAL EVALUATION AND CURE CYCLE

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ABSTRACT

Dynamic dielectric analysis (DDA) has been used to study curing polymer systems and thermoplastics. Measurements have been made over a frequency range of sic decades. This wide range of frequencies increases the amount of information which can be obtained. The data is analyzed in terms of the frequency dependence of the complex permittivity ε^*, specific conductivity $\sigma(\text{ohm}^{-1}\text{cm}^{-1})$ and the relaxation time τ, parameters which are characteristic of the cure state of the material and independent of the size of the sample.

Dynamic dielectric measurements have been used to monitor polymer processing in UDEL-P1700, LARC-160, polyphenyl quinoxaline (PPQ) and Epon 828 cured with Agent U. Dynamic dielectric measurements have been correlated with viscosity for the polysulfone thermoplastic UDEL-P1700 and with viscosity and ultrasonic measurements on the DGEBA type epoxy Epon 828 cured with Agent U. The experimental results suggest that when ionic processes dominate the dielectric response, the intensive property σ is a good monitor of the resin's viscosity. The results show that the dielectric relaxation time τ can be used to monitor the state of the system and the extent and rate of the reaction. Solvent evolution can also be easily observed.

DYNAMIC DIELECTRIC ANALYSIS: NONDESTRUCTIVE MATERIAL EVALUATION AND CURE CYCLE MONITORING

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ABSTRACT

Dynamic dielectric analysis (DDA) has been used to study curing polymer systems and thermoplastics. Measurements have been made over a frequency range of six decades. This wide range of frequencies increases the amount of information which can be obtained. The data is analyzed in terms of the frequency dependence of the complex permittivity ε^*, specific conductivity $\sigma(\text{ohm}^{-1}\text{cm}^{-1})$ and the relaxation time τ, parameters which are characteristic of the cure state of the material and independent of size of the sample.

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INTRODUCTION

Dynamic dielectric measurements made over a wide range of frequency provide a sensitive and convenient means for monitorning the cure process in thermosets and thermoplastics. Dielectric measurements are of particular importance for quality control monitoring of the cure process in complex resin systems because dielectric relaxation is one of only a few instrumental techniques available for studying molecular properties in both the liquid and solid states. Furthermore, it is probably the only convenient experimental technique for studying the cure process continuously, that is, to examine the cure chemistry throughout the process of going from a monomeric liquid of varying viscosity to a cross-linked, insoluble, high temperature solid.

The major long-range objective of our research is to develop on-line dielectric instrumentation for quantitative nondestructive material evaluation and closed loop "smart" cure cycle control. The key to achieving this goal is to relate the chemistry of the cure cycle process to the dielectric properties of the polymer system by correlating the time, temperature, and frequency dependent dielectric measurements with chemical characterization measurements. Measurement of the wide variation in magnitude of the complex permittivity with both frequency and state of cure, coupled with chemical characterization work, have been shown in our laboratory to have the potential to determine: resin quality, composition and age; cure cycle window boundaries; onset of flow and point of maximum flow; extent of and completion of reaction; evolution of volatiles; T_g; crosslinking and molecular weight buildup (Ref. 1,2,3)

In this report dynamic dielectric measurements of the DGEBA epoxy and polyimide LARC-160 thermosets and PPQ and UDEL polysulfone thermoplastic resins have been made at series of frequencies from 5 to 5 x 10^6 Hz. Capacitance (C), and the conductance (G) were recorded. The complex permittivity (ε^*), an intensive property which is characteristic of the material's state of cure and independent of the amount of material measured, was calculated. The frequency dependence of ε^* was used to determine the conductivity, σ(ohm^{-1}cm^{-1}) and a mean relaxation time τ. σ, which is also an intensive variable and independent of sample size, was correlated with the viscosity in both the EPON and the UDEL systems. For the curing thermoset resins the dielectric results were taken during the polymerization reaction.

EXPERIMENTAL

Dynamic dielectric measurements were made using a Hewlett-Packard 4192A LF Impedance Analyzer controlled by a 9826 Hewlett-Packard computer. The resin was cured in a 3" mole placed between thermostated heating plates. The time-temperature profile of the mold was controlled by a program in the computer. The layup consisted of a number of layers of Kapton to insulate the porbe from the metal mold, a probe which can be inserted directly between layers of polymer resin and further layers of Kapton between this and the mold top. An iron-Constantan thermocouple was attached directly to the mold and the temperature measured by a Keithley 179 TRMS Digital Multimeter. Measurements of capacitance (C) and conductance (G) at frequencies from 5 to 5 x 10^6 Hz were taken at regular intervals during the cure cycle and stored on a computer disk. The complex permittivity was calculated for each of these measurements. The temperature was also recorded for each measurement. Plots of the results were prepared from the stored data and were plotted using a Hewlett-Packard 7475A 6 pen plotter.

The viscosity measurements were made on a Rheometrics System IV dynamic mechanical spectrometer in the parallel plate mode. The ultrasonic measurements were made using a pulse echo apparatus (5 mHz). (Ref. 4)

Samples of PPQ, UDEL-P1700 and Epon 828 plus curing agent U were supplied by NASA-Langley Research Center.

LARC-160 was prepared as described elsewhere. (Ref. 2)

RESULTS AND DISCUSSION

Measurements of C and G were used to calculate the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$

$$\varepsilon' = \frac{C\ \text{material}}{C_o} \qquad (1)$$

$$\varepsilon'' \quad \frac{G\ \text{material}}{C_o 2\pi f}$$

This calculation is possible when using a probe whose geometry is invariant over all measurement conditions. Both the real and the imaginary components of ε^* can have a dipolar and an ionic component (Ref. 5).

$$\varepsilon' = \varepsilon_d' + \varepsilon_i' \qquad (2)$$

$$\varepsilon'' = \varepsilon_d'' + \varepsilon_i''$$

The dipolar component arises from rotational diffusion of molecular dipolar moments. In its simplest form, the polar component's frequency dependence is represented by a single relaxation time τ and

$$\varepsilon_d' = \frac{\varepsilon_o - \varepsilon_\infty}{(1+\omega^2\tau^2)} + \varepsilon_\infty$$

$$\varepsilon_d'' \quad \frac{(\varepsilon_o - \varepsilon_\infty)(\omega\tau)}{(1+\omega^2\tau^2)}$$

where ε_o and ε_∞ are the limiting low and high frequency values of ε_d. The rate of rotational diffusion of the polar moments is characterized by the relaxation time τ. In most systems, a distribution of relaxation times is observed. The distribution is due to a combination of molecular phenomena including the presence of more than one polar species, the assymetric shape of the polar group and intra- and intermolecular forces. The intermolecular forces determine the extent to which the motion of the dipoles are correlated with each other.

The ionic component, ε_i', often dominates ε_i. The presence of mobile ions gives rise to localized layers of charge near the electrodes. Since these space charge layers are separated by very small molecular distances on the order of Å, the corresponding space charge capacitance can become extremely large, with ε' on the order of 10^6. Johnson and Cole, while studying formic acid, derived emperical equations for the ionic contribution to ε*. In their equations, these space charge ionic effects have the form

$$\varepsilon_i' = C_o Z_o \sin\left(\frac{n\pi}{2}\right) \omega^{-(n+1)} \left(\frac{\sigma}{8.85 \times 10^{-14}}\right)^2 \qquad (4)$$

where $Z^* = Z_o(i\omega)^{-n}$ is the electrode impedance induced by the ions and n is between 0 and 1. (Ref. 5, 6,7) The imaginary part of the ionic component has the form

$$\varepsilon_i'' = \frac{\sigma}{8.85 \times 10^{-14}\omega} - C_o Z_o \cos\left(\frac{n\pi}{2}\right) \omega^{-(n+1)} \left(\frac{\sigma}{8.85 \times 10^{-14}}\right)^2 \qquad (5)$$

where σ is the conductivity ($\text{ohm}^{-1}\text{cm}^{-1}$), an intensive variable, in contrast to conductance G(ohm^{-1}) which is dependent upon cell and sample size. The first term in eq. 5 is due to the D.C. conductance of ions translating through the medium. The second term is due to electrode polarization effects. The second term becomes increasingly significant as the frequency of measurement is decreased.

In this paper we will focus on three ways in which dynamic dielectric measurements can be used to monitor the cure reaction. In assessing each method, it is important to remember that any procedure which is developed and used for cure process monitoring is, in general, unique to a particular resin system and/or application. The essential requirement is that the molecular basis for the frequency dependence of the dielectric signal be understood. Using this information we will show how the ionic contribution ε_i^*, the dipolar contribution ε_d^* and the magnitude of ε* can be used for cure cycle monitoring.

The first system to which we will apply these three dielectric analysis techniques is the polysulfone thermoplastic UDEL-P1700. Figure 1 is a plot of conductance and capacitance at 5 kHz during a 2°/min ramp to 280°. The variation in C and G clearly shows that the magnitudes of both C and G are a sensitive means of detecting the onset of softening at ≈150° and detecting the glass transition at 190°. The spike in the conductance curve virtually coincides with the temperature of the glass transition. However care must be taken before using this peak as the glass transition point without first understanding the molecular basis for the frequency dependence of the dielectric properties in the UDEL polysulfone system. For example the position of the conductance spike varies with frequency.

Figures 2 and 3 show that plots of ε' and ε'' are complex functions of frequency and temperature. Their molecular basis can be understood if we separate out the ionic and dipolar contributions to ε' and ε''. Then the temperature dependence of ε' and ε'' can be used with equations which model the frequency dependence of ε_i and ε_d (eqs. 3,4,&5) to determine processing properties.

Using equation 5, and assuming the second term is small compared to the first, the specific conductivity σ has been determined from the frequency dependence of ε''. The specific conductivity σ is a molecular parameter which is independent of sample size. It is a function of the ease with which charged particles translate through the polymer. As such it is a sensitive measure of the viscosity and the structure of the polymer as the polymer's properties change with temperature. (Fig. 4) Figure 5 is a plot of σ versus viscosity. For polysulfone the product $\sigma\eta$ is a constant at temperatures above Tg. As seen in figures 4 and 5, frequency dependent dielectric measurements may be used to monitor the viscosity quantitatively, during processing.

Figure 6 is a plot of the dipolar contribution to ε'' at several temperatures. The plots of ε_d versus frequency show peaks which move from lower frequencies to higher frequencies as the temperature increases. The reciprocal of the frequency for ε_d'' (max) is a characteristic relaxation time τ for rotational diffusion of dipoles. Like σ it is a sensitive measure of viscosity and molecular structure of the resin. In turn τ like σ can be used to monitor the state of a thermoplastic polymer system. In Figure 6, we observe that the dipolar relaxation time τ becomes increasingly shorter (ε''_{max} occurs at successively higher frequencies) as the viscosity decreases and the temperature increases.

The second system we examine is the polyimide resin LARC-160. Here we observe the dynamic time-temperature cure process. Previous work has shown that LARC-160 polymerization occurs in 3 steps: first, imidization of the nadic group and the amine; second, imidization of the tetracarboxylic acid-ester with the amine; third, addition-crosslinking of the nadic end-capped oligomers (See Figure 7) Figure 8 plots ϵ' versus time for several frequencies.

The figure shows an initial rapid rise in ϵ' due to the onset of flow and the subsequent decrease in viscosity with temperature at 80°. The rate of increase in ϵ' with time decreases due to the onset of imidization of the nadic-amine monomers. At 100° the rapid rise in ϵ' resumes indicating the nadic imidization is nearly complete. At 120° this rapid rise in ϵ' ends and ϵ' begins to decrease with time. At this point the onset of imidization of the benzophenone tetracarboxylic acid-ester and the amine has begun. This chain propogating reaction increases the molecular weight, driving the viscosity up, and ϵ' down. The point at which the reaction is complete may be monitored by observing the time needed for ϵ' to achieve a steady state value. From Fig. 9 it can be seen that the reaction at 180° is still going on at the end of the 1.5 hr hold. The high temperature addition reaction can be monitored as shown in Figure 9. Completion of the reaction during the 280° hold and the 330° hold can be determined from the ϵ' versus time plot. An additional use of the time-temperature dependence is seen in Figure 10. Figure 10 shows ϵ' versus time-temperature for LARC-160 resin stored for varying lengths of time in a refrigerator. Over extended storage periods, the extent of the imidization reaction, and the associated cure cycle processing properties are advanced in time. These observations revealed by the dielectric data are in agreement with other chemical characterization studies. (Ref. 2) These results show that changes in magnitude of dynamic dielectric properties are probes of properties such as the onset of flow, onset of reaction, and reaction completion as well as the effects of resin age.

The third system to which we apply dielectric analysis is the DGEBA type epoxy resin Epon 828 cured with Agent U. Figures 11 and 12 plot ϵ' and ϵ'' at three frequencies versus time during a 30° isothermal cure. The magnitude of ϵ' and ϵ'' clearly show that the reaction is still not complete after 200 min. Figure 13 is a plot showing the variation of the modulus G* and the viscosity over the first 100 minutes of the 30° isothermal cure. It is interesting to point out that the modulus and viscosity have moved beyond the measurement range of the parallel plate mode of the rheometer after 100 minutes. Thus while the mechanical rheometer in this mode cannot monitor further cure, dielectric techniques can. The fact that further cure is occuring is verified by examining ultrasonic measurements (Fig. 14) of the variation of the modulus in both a shear and storage mode over 500 minutes. Thus the magnitude of ε^* does monitor the cure process continuously over the 400 minutes needed for complete reaction. During this period the resin goes from a moderately viscuous fluid ($\sim 10^2$ poise) to a hard brittle solid ($\sim 10^9$ poise).

As discussed for polysulfone, the frequency dependence of ε^* can be used to separate the ionic and dipolar contributions to ε^*. In turn the molecular parameters σ and τ which characterize the ionic and dipolar processes for the epoxy resin can be determined. Figure 15 plots σ versus η for Epon 828 + U. Figure 15 shows that there are two distinct relationships between σ and η. A sharp break occurs when the epoxy gels, often associated with the point $\eta = 10^3$ poise. Up until this point, σ is strongly dependent on η. After gel σ is now sensitive to the effect of increases in crosslink density on the ions' rate of translational diffusion. Thus its functional dependence on η differs markedly from the pre-gel stage.

In the epoxy resin system, DDA can be used to monitor the time-temperature dependence of the polymerization process. The time it takes for the dipolar relaxation time $\tau = \frac{1}{2\pi f_{max}}$ to occur can also be used to monitor the extent or stage of the epoxy reaction. Table I reports the elapsed time for the values of $\tau = \frac{1}{2\pi 5x10^3}$ and $\tau = \frac{1}{2\pi 5x10^5}$ to occur. A relaxation time $\tau = \frac{1}{2\pi 5x10^3}$ for the resin corresponds to a higher viscosity and a more advanced reaction state than τ(500 kHz). Table I shows that the elapsed time until the resin attains this relaxation time is an extremely sensitive means for detecting small differences in formulation and the precise time for a particular extent of reaction to occur.

A final observation on the value of dielectric measurements to polymer processing is shown in Figure. 16. The dissipation D is the ratio of

$\varepsilon''/\varepsilon'$ and as such is an extremely sensitive monitor of physical and chemical changes in the resin and their subsequent affect on ε'' and ε'. As seen in Figure 16, it can be used to detect and monitor the evolution of volatiles. The xylenes vaporize from the polyphenyl quinoxaline film at their boiling point. The m-cresol, which interacts more strongly with the polymer, is released 50° above its boiling point.

We have examined the use of three dielectric techniques to determine ionic and dipolar molecular parameters and thereby to monitor the viscosity and extent of reaction in representative thermoplastic and thermoset resins. Several cautionary remarks need to be made. First the use of bulk measurements of C or G are dependent on variations in sample size and geometry and are not intensive properties of the material as are ε^*, σ and τ. Measurements which rely on a single frequency or a small range of frequencies will in general not correlate with a particular processing property except over a narrow time-temperature range of the cure process. This is because the different molecular processes affecting the ions and dipoles are moving in and out of the time scale of the measurement window. Third, measurements at low frequencies (<10 Hz) become increasingly sensitive to electrode impedance effects. Thus, as the frequency becomes lower, a larger portion of ε^* is determined by electrode polarization rather than the ionic and dipolar dielectric properties of the bulk material.

CONCLUSIONS

Previous work has shown that dynamic dielectric equipment can be constructed and used to monitor the cure process in a variety of thermoplastics and thermosets, on the pure resin or resin/graphite or glass cloth, over temperatures up to 750°F and covering values of ε'' from 10^{-3} to 10^{6} Hz (Ref.1-3,8-11). Inthis paper, we have discussed applications of the use of the magnitude of ε^* and two molecular parameters, the ionic conductivity σ and the dipolar relaxation time τ to monitor and measure the viscosity, the state of the system and the extent of the reaction as a function of time-temperature for representative thermoplastics and representative epoxy and polyimide thermosetting resins. The results show dynamic dielectric analysis is an extremely powerful and convenient technique for nondestructive quality control monitoring of cure processing.

ACKNOWLEDGEMENTS

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Table I

Epon 828: Agent C

Maximum in ϵ'' vs. time at	100:15	100:24.3	100:25	100:35
5 KHz	161 mins.	89 mins.	84.9 mins.	26.1 mins.
500 KHz	55 mins.	45 mins.	43 mins.	21.7 mins.
difference	86 mins.	44 mins.	41.9 mins.	4.4 mins.

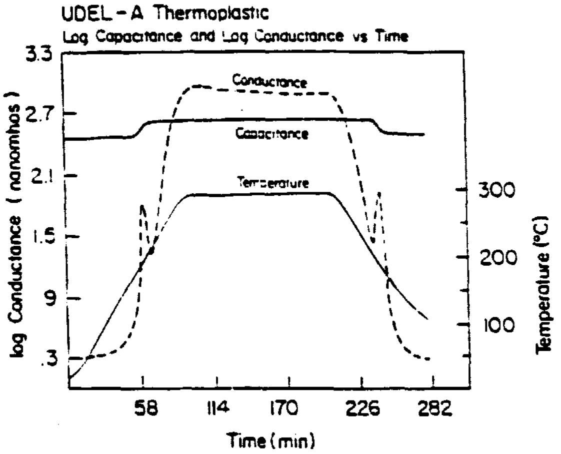

Fig. 1. Log Capacitance and Log Conductance vs Time for the thermoplastic UDEL P-1700. The temperature was ramped to 280°C and held for 2 hrs. A portion of the cool-down curve is also plotted.

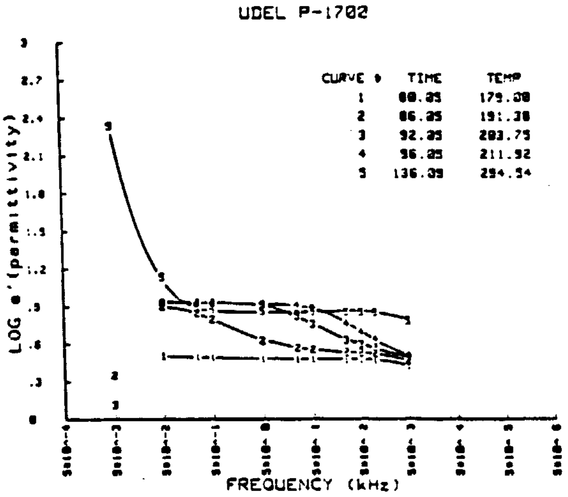

Fig. 2. Log ε' vs frequency (kHz) for UDEL at selected times during a heating ramp to 320°C.

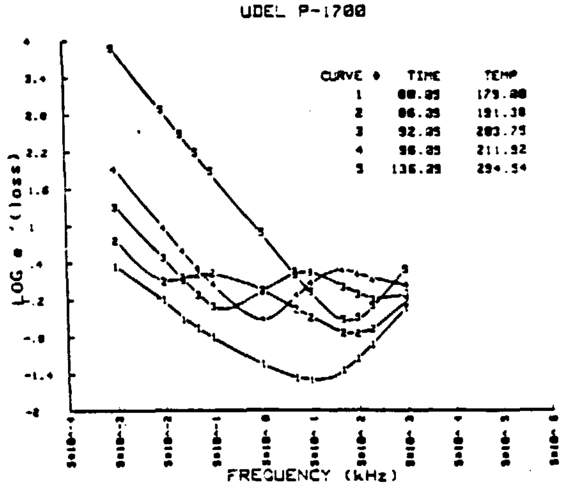

Fig. 3. Log ε" vs frequency (kHz) for UDEL at times and temperatures of Fig. 2.

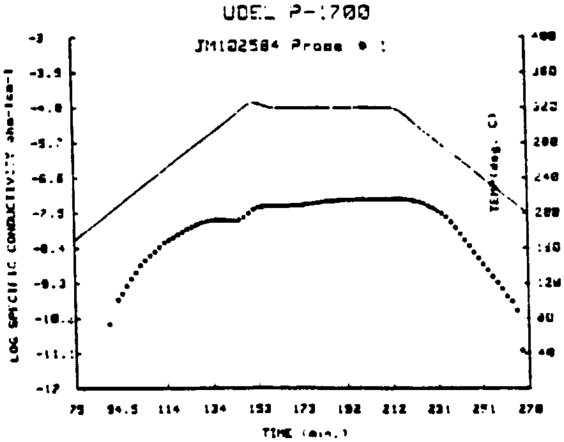

Fig. 4. Log Specific Conductivity vs time for a temperature ramp to 320°C, a 20 min. hold, and cool-down to 200°C.

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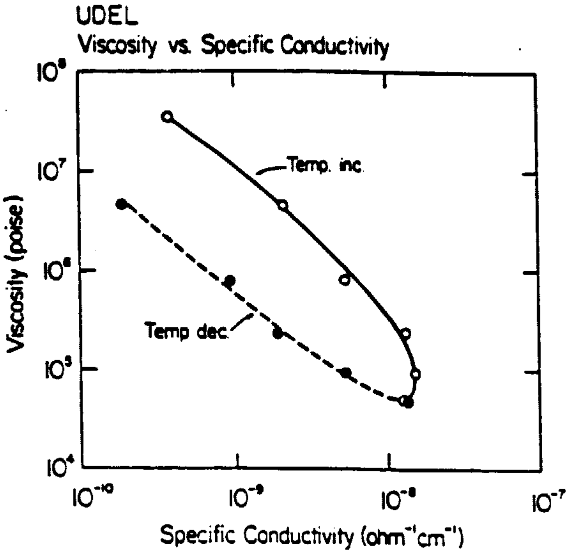

Fig. 5. A comparison of viscosity and specific conductivity for UDEL as the polymer is warmed then allowed to cool. The specific conductivity was taken from Fig. 4 at points which correspond in temperature to temperatures at which viscosity data was taken. Viscosity was measured on a Rheometrics System 4 Rheometer.

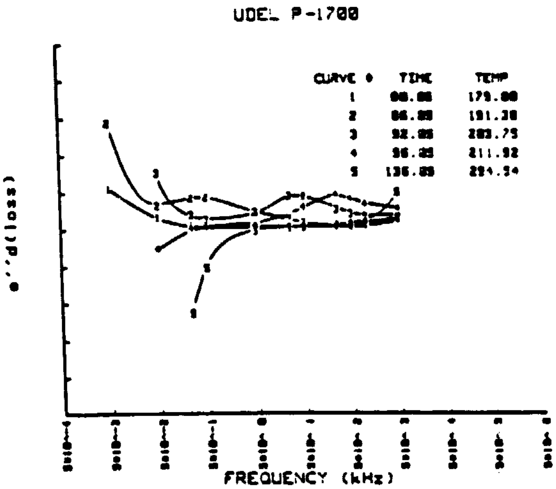

Fig. 6. The dipolar loss, ε_d'' vs frequency for UDEL at the temperatures of Figs. 2 and 3. ε_d'' was calculated neglecting the second term in eq. 5. Thus, at the low frequency end of the high temperature curves (curves 4 and 5) a precipitous drop in "ε_d''" denotes the onset of significant electrode polarization effects.

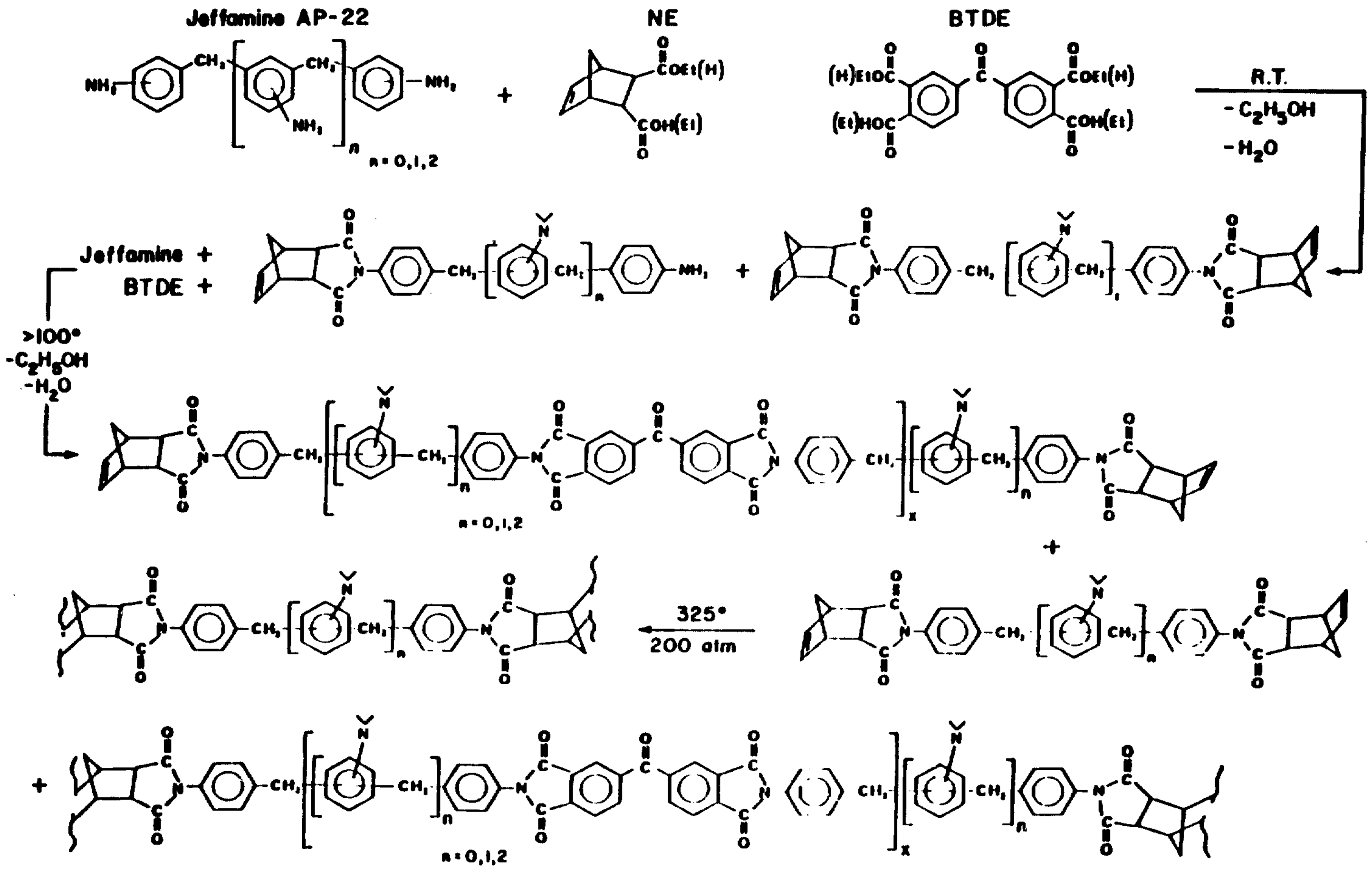

Fig. 7. Reaction sequence for polymerizing LARC-160.

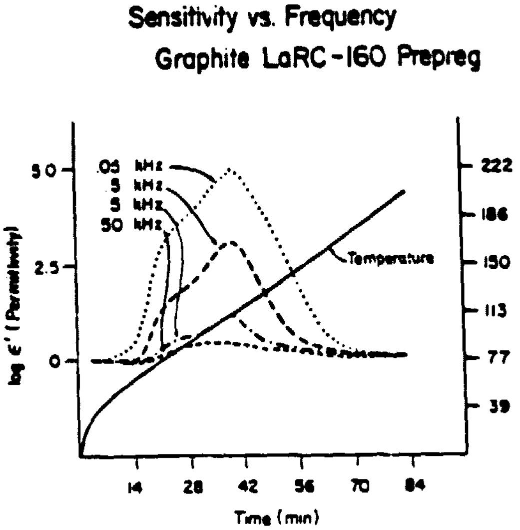

Fig. 8. Log ε' vs time for imidizing LARC-160.

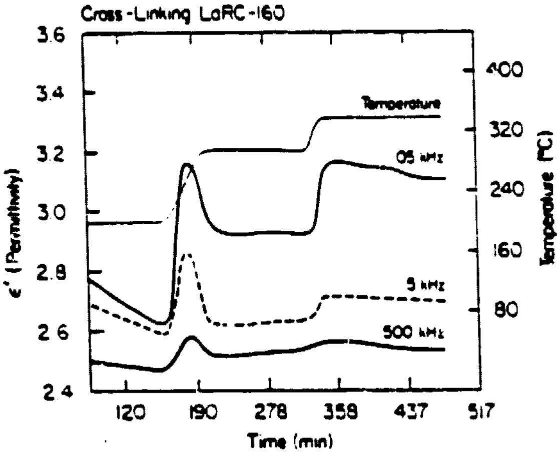

Fig. 9. ε' vs time for curing LARC-160 during 180° hold and subsequent crosslinking temperature cycle.

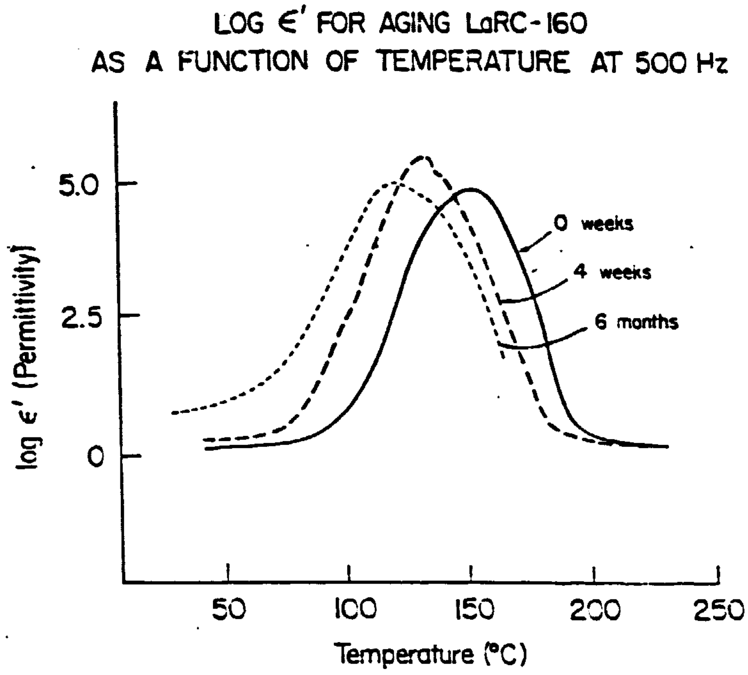

Fig.10. Log ε' vs temperature for imidizing LARC-160 during 2°/min temperature ramp. The uncured resin was stored at 5°C for times indicated in the drawing.

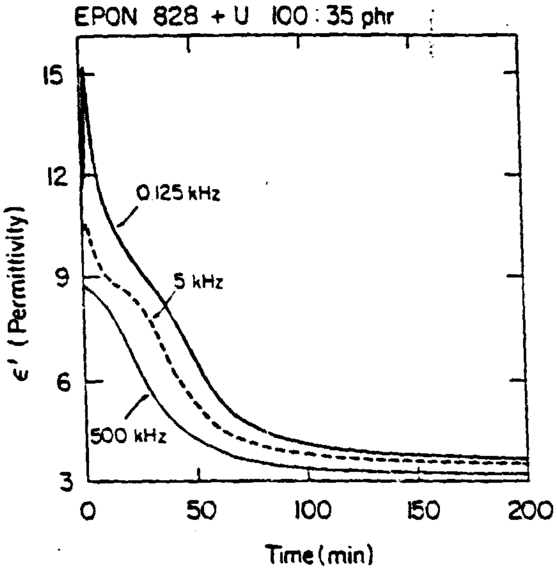

Fig.11. ε' vs time for EPON 828 cured with Agent U (100:35 phr) at 30°C. Three representative frequencies are shown.

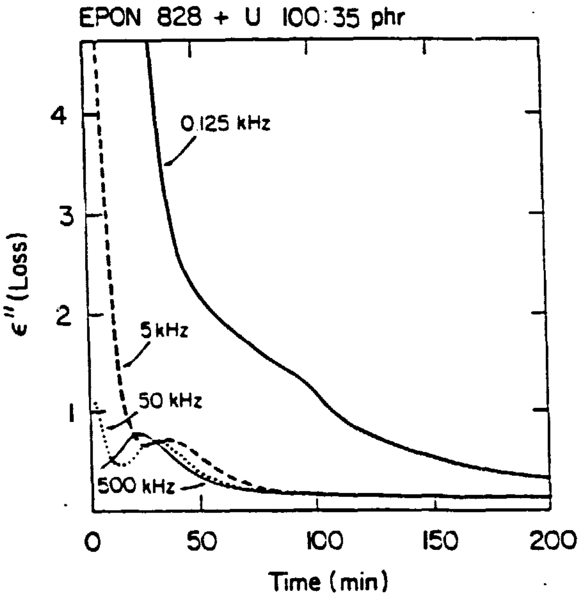

Fig.12. ε" vs time for the same sample as in Fig. 11. Results for 4 frequencies are shown.

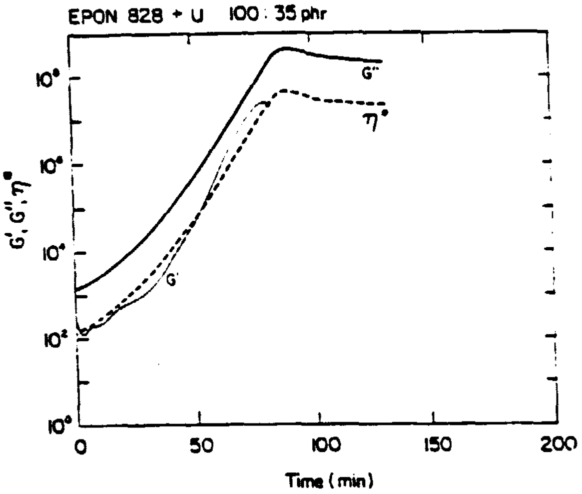

Fig.13. The real and imaginary parts of the modulus and the complex viscosity for EPON + Agent U under the same conditions as above.

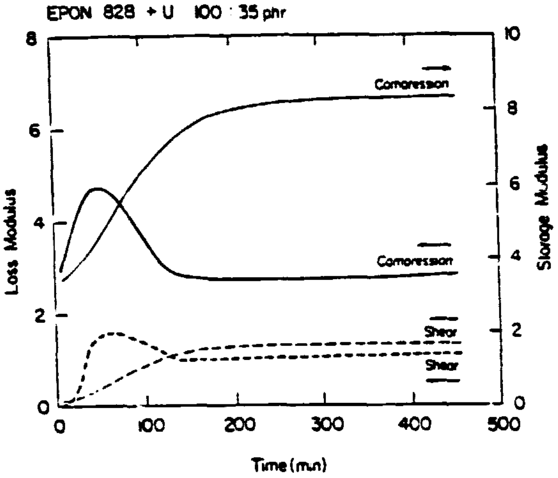

Fig.14. The loss and storage modulus for EPON 828 + Agent U under conditions as above.

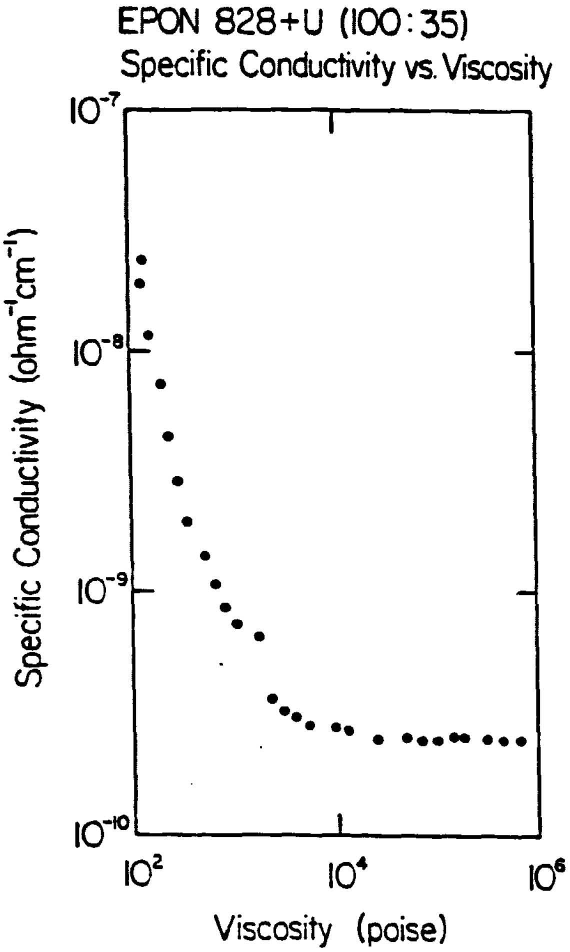

Fig.15. A comparison of Specific Conductivity from DDA data (Fig.12) with Viscosity from Rheometrics data (Fig.13) for EPON 828 + Agent U.

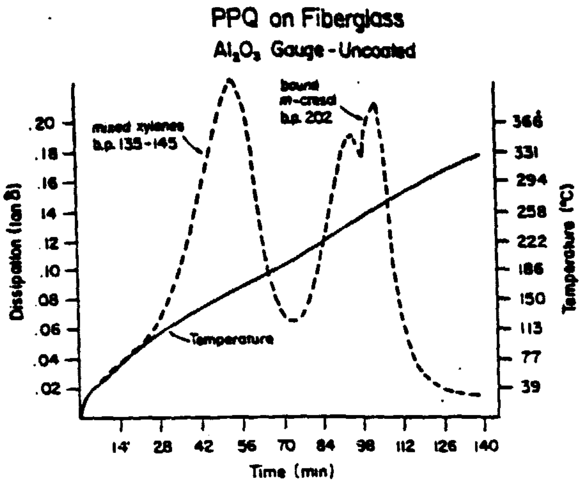

Fig.16. Dissipation vs time for PPQ film heated with the temperature ramp shown in the drawing.