

Dynamic Mechanical Properties of Supported Polymers. II. Application of the Torsional Braid Technique to the Study of the Curing and Stability of Resins*

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INTRODUCTION

This research is part of a more general study of supported polymers in which changes in rigidity, which accompany polymeric transformations, are being investigated. The concept of supported polymers extends the range of investigation by dynamic mechanical methods to conditions under which polymers are not self-supporting. Special fabrication of specimens is eliminated, while small amounts of sample (less than 0.1 g.) are required for such tests. This communication describes the application of the torsional braid technique^{1,2} to the study of curing and stability of commercial resins. The applicability of this technique to the study of chemical^{1,3} and physical transformations^{1,2,4} has been demonstrated.

Prior to torsional braid analysis (TBA), a preliminary examination of a resin from the viewpoint of its heat-resistant properties usually consisted of conducting weight loss experiments, such as thermogravimetric (TGA) and isothermal gravimetric analyses, in inert and oxidizing atmospheres. Typically the results were complemented by those of differential thermal analysis (DTA) which detects endo- and exothermic processes, and by thermal softening tests.⁵ Small quantities of material are required for these preliminary procedures. However, subsequent examination involves the fabrication of specimens in the form of films, castings, moldings, or reinforced laminates for evaluation by standard engineering testing procedures. Such evaluation, as a result of the generally destructive nature of these testing methods, is time-consuming and involves large quantities of material.

A disadvantage of the preliminary testing procedures is that their results have little relationship to the properties which are measured in the larger, fabricated specimens. There is a need for a preliminary testing procedure, using small amounts of sample, which can be more meaningfully related to

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the properties of the final product. Torsional braid analysis represents an attempt to satisfy this need.

EXPERIMENTAL

Methods

The basic torsional braid apparatus which has been previously described^{1,2} was employed throughout this investigation. A modified torsional pendulum was employed in which the vertical specimen shaft consisted of a braid of glass fibers which was impregnated with the polymeric material under investigation. In principle, any changes in the mechanical rigidity of this composite would be reflected by changes in frequency of the freely oscillating inertial mass of the pendulum. By

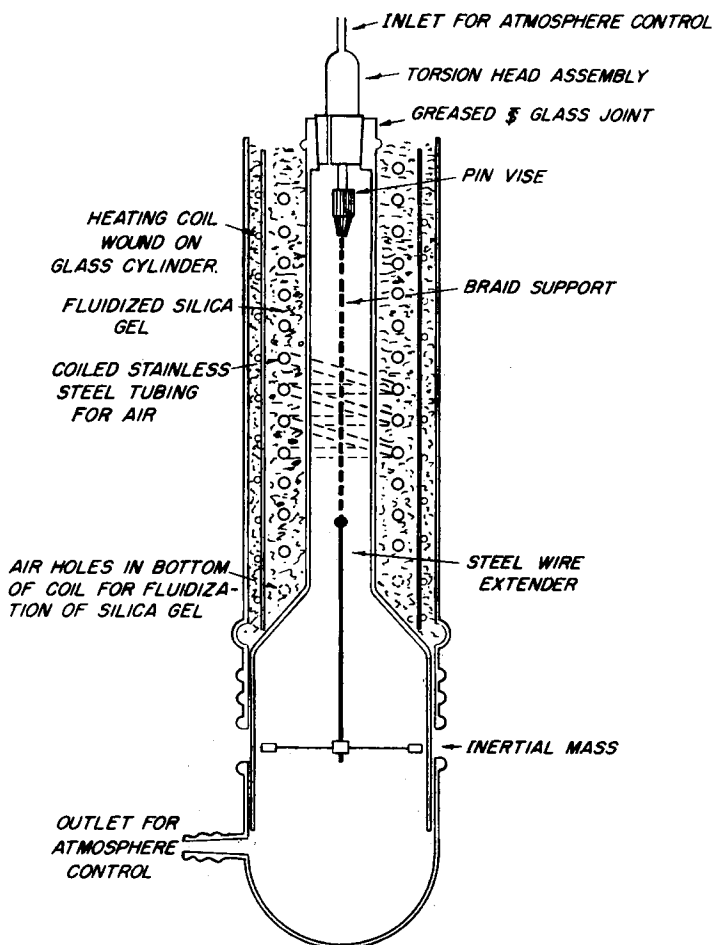


Fig. 1. Torsional braid apparatus.

expressing the calculated rigidity modulus G relative to some arbitrary value G_0 in each experiment, a relative rigidity parameter was derived. This parameter partially overcame the difficulties which were encountered in defining the geometry of the system. This treatment of the data assumes the mechanical damping of the system to be negligible. Experimentally, the relative rigidity parameter reduces to P_0^2/P^2 , where P_0 and P are the periods of oscillation at the reference and measured conditions, respectively. Unless stated to the contrary the basis for the relative rigidity parameter throughout this work was taken to be the rigidity at room temperature, G_{rt} , of the cured or pyrolyzed resins.

For high temperature experiments a fluidized-by-air bed of silica gel was used as the heat transfer medium (Fig. 1). This method had the advantage of excellent temperature control ($T \pm 1^\circ\text{C}.$) and temperature distribution profile, throughout a range from below room temperature to above $500^\circ\text{C}.$ The use of a fluidized bed in place of hot circulating fluids had the further advantage of safety.

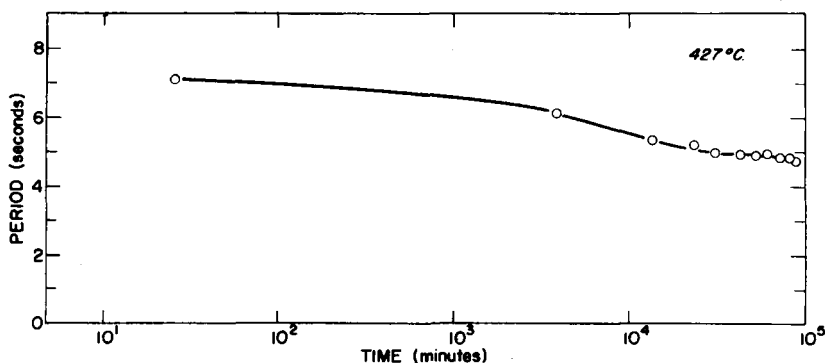


Fig. 2. Isothermal ($427^\circ\text{C}.$) behavior of glass braid.

The inert substrate which was used as the support was braided glass yarn. This was obtained by braiding, by hand, three yarns, each designated ECE 225 $\frac{1}{3}$ 4.4S, from heat-cleaned glass cloth (181-V12 of United Merchants Industrial Fabrics, New York, New York). Each braid consisted therefore of 1836 filaments. The variations of the rigidity of such a braid with temperature (to $485^\circ\text{C}.$) was found to be negligible. Isothermally (at $427^\circ\text{C}.$) a lowering of the period of vibration was apparent. Figure 2 presents this latter behavior as a function of time. However, the effect was not considered significant enough to alter the interpretation of the isothermal experiments.

Unless stated to the contrary, the experiments were performed in a nitrogen atmosphere (prepurified cylinder grade, Air Reduction Company) at atmospheric pressure. Air (water pumped breathing air, Air Reduction Company) was used at atmospheric pressure and at a flow rate of 25–50 ml./min. for oxidation.

Thermal softening experiments, which relate the rigidity as a function of rising temperature, were carried out over a period of 4 hr. The rate of rise of temperature was unprogrammed, but decreased exponentially with time.

Condensable products of pyrolysis collected in the lower (room temperature) part of the apparatus, but were not examined.

Validity of Technique

The validity of the technique rests on the assumptions that the substrate is mechanically inert, and further that it does not interact with the material which it supports. It seems apparent that an approach to the first condition is to have the substrate made from materials the physical properties of which change little throughout the conditions of the experiment. Thus glass and quartz, with lower coefficients of thermal expansion, would be expected to be better suited than metal in experiments where wide fluctuations in temperature occur. The contribution of the support to the rigidity of the composite is less when a braid rather than a single rod is used. An examination of the data presented shows that the rigidity of the cured resin-glass braid composite is at least a hundred times that of the uncoated braid. The employment of a braid rather than a filament permits the polymer to impregnate the support such that a more or less uniform rod ensues with about equal volume fractions of polymer and support. During the cure the braid adds reinforcement to the system. It was previously demonstrated² that under certain limitations, such experiments conformed to mathematical analysis as a filled polymer.

Throughout the measurements, the maximum torsional strain which was induced into the supporting member was less than 0.5%. Periods of the induced oscillations ranged from about 10 sec. for curing studies to about 0.5 sec. for pyrolytic studies. Modulus dispersion due to frequency variation was not considered important for a qualitative interpretation of the results. Since reproducibility was consistently achieved it was felt that the effects of fatiguing were negligible.

Materials

Three commercial thermosetting resins were investigated and in this work are designated as a phenolic, an unsaturated polyester and as a phosphonitrilic. The phenolic is a heat-resistant ablative phenolic resin, the product of U. S. Polymeric Chemicals, Inc., Stamford, Connecticut. The polyester is marketed as Laminac 4232 resin (American Cyanamid Company). The formulation contained poly(ethylene maleate) and triallyl cyanurate, and could be set by heating with 1% of benzoyl peroxide as catalyst. The phosphonitrilic resin is marketed as Dynalac-HU (General Dynamics Corporation, San Diego, California).

TORSIONAL BRAID STUDIES

A. Cure

The polymerization of each resin was monitored on the braid for the conditions of time and temperature which the manufacturer recommended

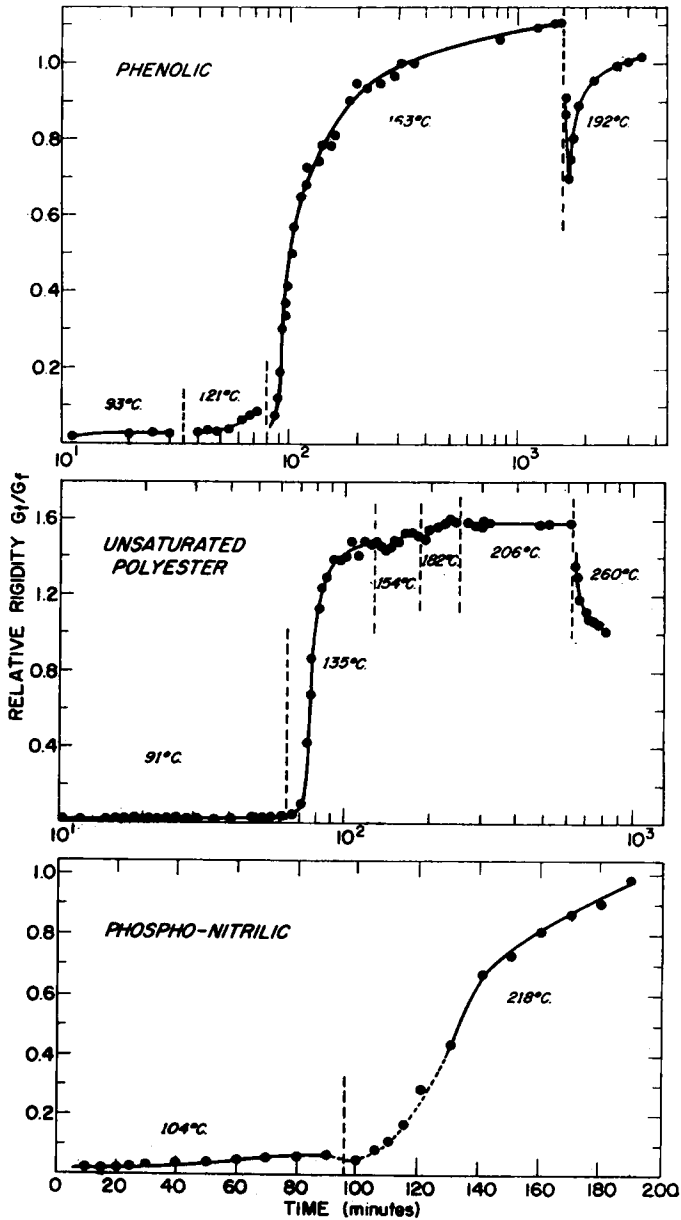


Fig. 3. Curing behavior of thermosetting resins.

for the formation of castings. In Figure 3 the curing behavior of the resins is presented in "finger print" form, in terms of changes in relative rigidity as G_t/G_f . Here G_f is the rigidity modulus of the cured product at the temperature of the final curing isotherm (reference state), while G_t is the rigidity modulus at time t . That the rigidity has not levelled off at the end of the cure cycle illustrates the arbitrary nature of commercial curing programs. It is well known that plastics technology lacks a reliable means for measuring cure.⁶ Studies using this present technique should permit the establishment of reliable curing programs, thus creating more durable resin products. Furthermore, the laborious empirical method for determining optimum curing conditions in new systems could be curtailed.

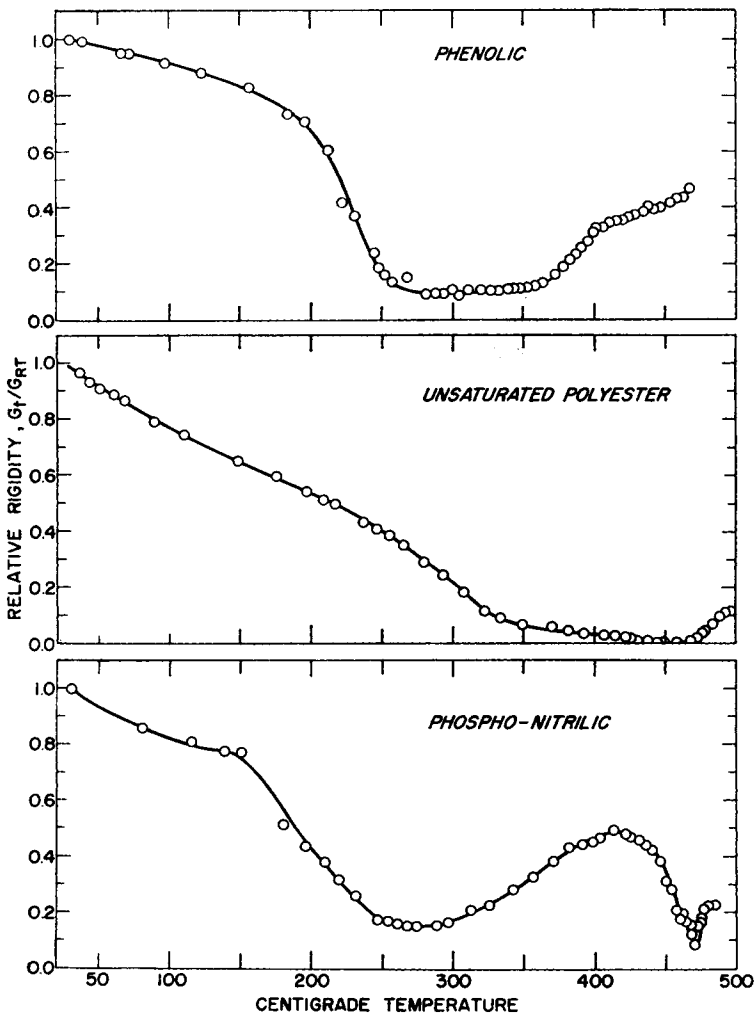


Fig. 4. Thermal softening of cured resins.

The vertical dotted lines between the successive solid isotherms of Figure 3 mark the time intervals taken to raise the temperature from one isotherm to another. It is apparent, for example after consideration of the last (192°C.) isotherm of the curing behavior of the phenolic, that at the beginning of a new isothermal treatment, thermal softening often precedes further thermal cure.

The final curing stage (260°C.) of the polyester was characterized by a drastic decrease in rigidity. This behavior may be attributed to the triallyl cyanurate component which is known to isomerize at this temperature. A preliminary communication³ reported a difference in thermomechanical behavior between poly(triallyl cyanurate) and poly(triallyl isocyanurate) which was attributed to an isomerization reaction of the former.

It should be emphasized that in these TBA experiments, since the small quantity of sample is spread over a relatively large area, the effect of reaction exotherms is generally negligible. The recognition of this fact is necessary when results from TBA experiments and bulk experiments are compared.

B. Thermomechanical Behavior

The thermal softening characteristics of the resins (after the recommended cure) are presented in Figure 4. All three resins soften, losing half of their initial rigidity at $200 \pm 25^\circ\text{C}$. However, an examination of the thermal softening curves indicates that the employment of a different

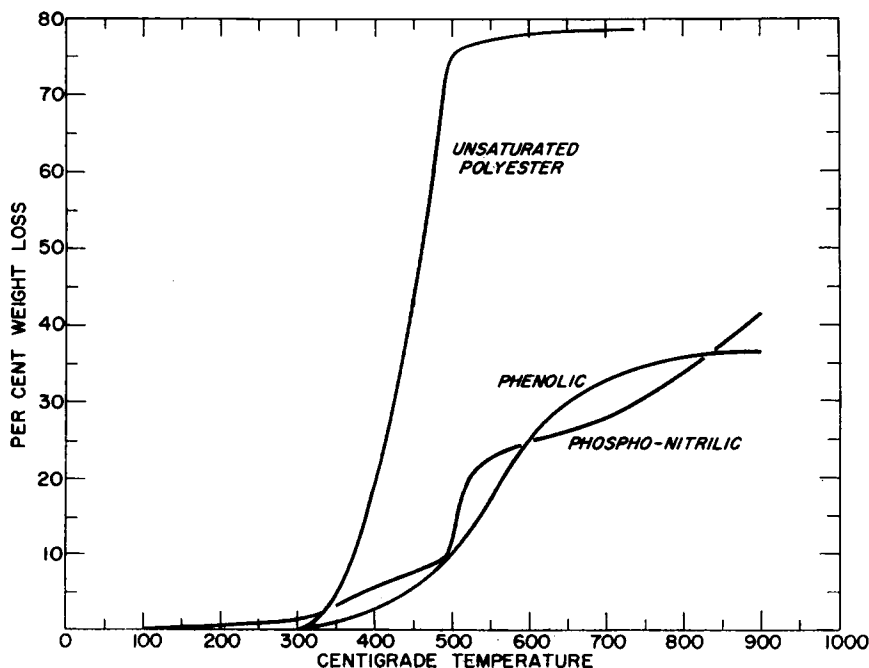


Fig. 5. Thermogravimetric analysis in nitrogen of thermoset resins.

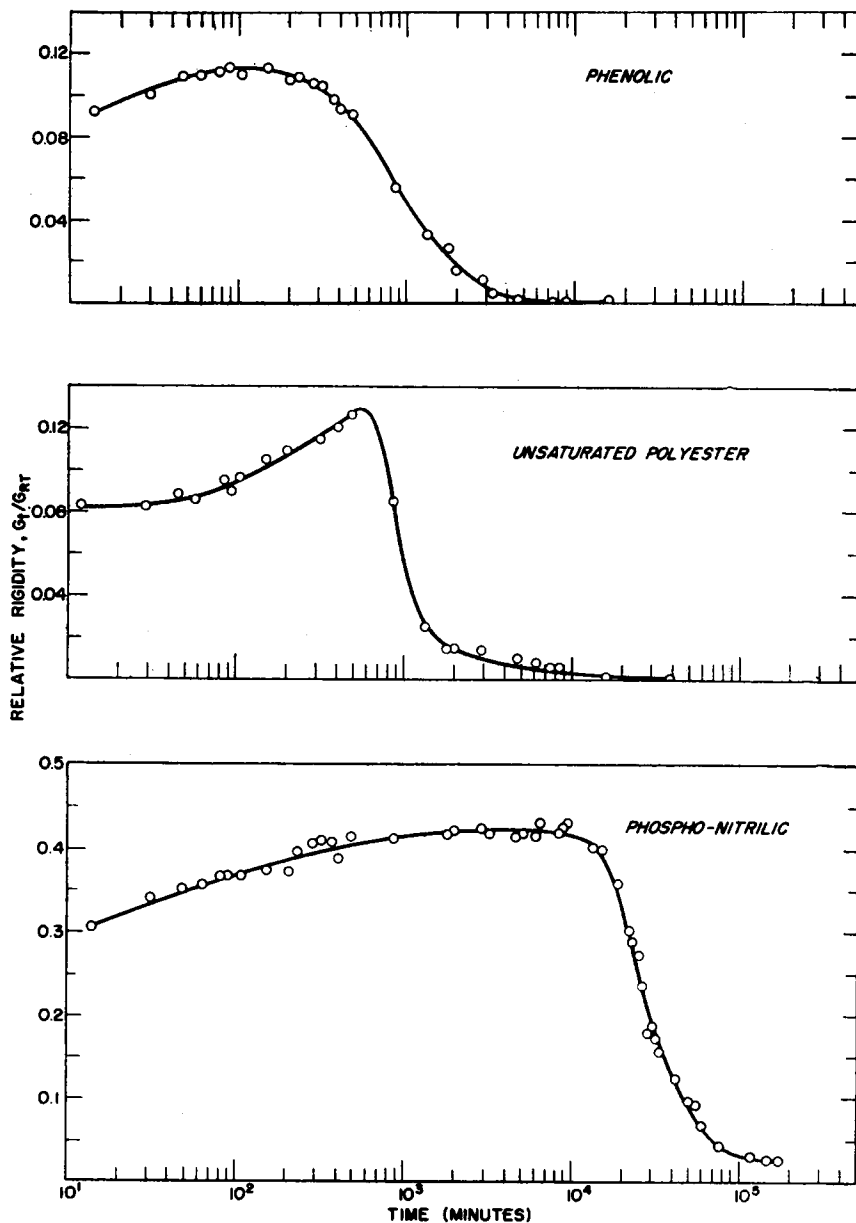


Fig. 6. Isothermal (344°C.) oxidation of cured resins.

curing cycle would be beneficial to the phenolic and to the phosphonitrilic resins. On raising the temperature, these two resins softened and subsequently increased in rigidity. This latter behavior was paralleled by a weight loss. Figure 5 represents the thermogravimetric analyses under a nitrogen atmosphere. The phenolic and phosphonitrilic resins cure

by elimination reactions, and therefore part of the observed mechanical tightening is attributable to postcuring action. On the other hand it is quite obvious from thermogravimetric analysis and from the lowering of rigidity that under the conditions of this experiment the polyester decomposes before postcuring.

The phosphonitrilic resin, after the initial softening and subsequent tightening of the structure (to 400°C.), softened to about 470°C. and then hardened again. The last softening is interpreted as being the result of degradation which preceded formation of a pyrolyzed structure. The pyrolyzed structure was one with definite mechanical elasticity. The hypothesis of pyrolysis was supported by the difference between the electrical resistivities, 2.4×10^4 ohm-cm. at 25°C. for the pyrolyzed (in a manner represented by Fig. 4) phosphonitrilic braid composite, and the value of greater than 10^{14} ohm-cm. at 25°C. for the cured resin.

It is quite apparent that the measurement of thermomechanical behavior by TBA can be meaningfully employed in preliminary investigation of resin stability.

C. Isothermal Oxidation

The results of isothermal (344°C.) oxidation in air of these resins, cured according to the commercial recommendations (Fig. 3), are presented in Figure 6. The ultimate dominance of oxidative degradation becomes apparent at different times after preliminary tightening of the structures, and so it appears that under these conditions the phosphonitrilic is at least an order of magnitude more stable than the other resins. The method might well be employed in comparative studies of resin stability to environmental attack.

D. Mechanical-Electrical Monitor of Pyrolysis

Since the pyrolysis of the phosphonitrilic resulted in a material with relatively low electrical resistivity, the concurrent mechanical and electrical changes which accompanied pyrolysis were studied. The torsional braid apparatus was modified so that the coated braid was an integral part of an electrical circuit. This was accomplished by having the free end of the inertial mass (Fig. 1) carry a fine copper wire extension which dipped into a pool of mercury held at room temperature. The electrical circuit was completed through electrodes at the top and bottom of the apparatus, and incorporated an ohmmeter. The damping of the oscillations by the mercury was small, and so the sample could be subjected simultaneously to dynamic mechanical and electrical resistance testing.

The cured phosphonitrilic, on the glass braid, was heated to 427°C. and the subsequent electrical, as well as mechanical, changes which occurred isothermally at 427°C. were monitored. The results are presented in Figure 7.

The first minimum in the mechanical rigidity plot of Figure 7 corresponds to the last minimum (at 470°C.) of the thermal softening curve of Figure 4.

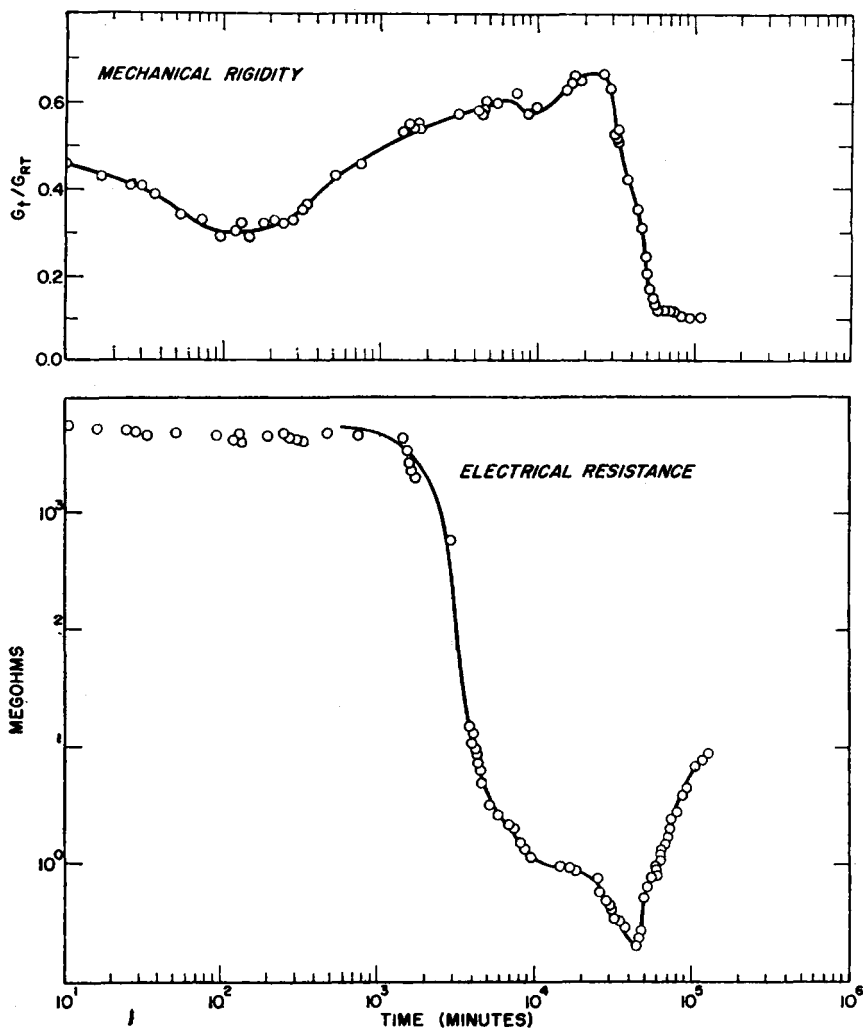


Fig. 7. Isothermal (427°C.) pyrolysis of phosphonitrilic resin.

The increase in rigidity, after this minimum, was attributed to the formation of a pyrolyzed continuum and, as would be predicted, is accompanied by a decrease in electrical resistance. Eventually, after several weeks at 427°C., the pyrolyzed continuum itself breaks down and apparently loses its continuity. The decrease in rigidity parallels in a general way the predictable increase in electrical resistance.

The limit of sensitivity of the ohmmeter was about 10^4 megohms. Therefore, the early stages of isothermal pyrolysis could not be followed with confidence. Hence, in this region, the data points of Figure 7 were left unconnected.

Further considerations of the electrical resistivity of the pyrolyzed phosphonitrilic resin were based on the assumption that the electrical

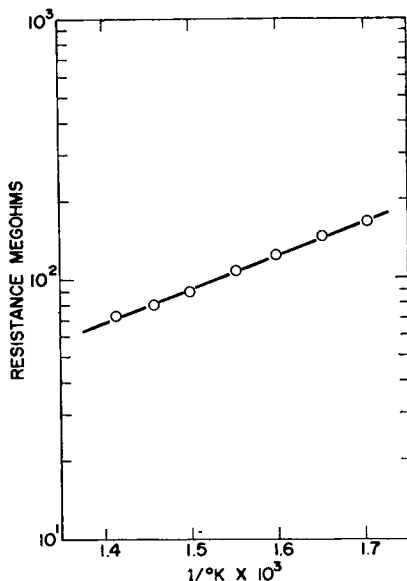


Fig. 8. Temperature dependence of the resistance of pyrolyzed phosphonitrilic resin.

conduction could be considered as a rate process.⁷ Hence the Arrhenius-type equation was invoked. The data of Figure 8 shows the temperature dependence of the pyrolyzed (27,700 min. at 427°C.) phosphonitrilic resin between 428 and 314°C. The energy of activation for electronic conduction was calculated to be 5.9 kcal./mole (0.256 e.v.).

E. Comparative Oxidation of Pyrolyzed and Normal Resin

Pyrolysis of the phosphonitrilic resin in an inert atmosphere produces a structure which differs from the normally cured resin in its electrical properties. The difference in structure is also apparent from thermo-mechanical studies. The thermal softening behavior of the resin after pyrolysis to 485°C. was characterized by the absence of maxima and minima. This is in contrast to the thermal softening behavior of the normally cured resin (Fig. 4).

Furthermore, a comparison of the oxidative behavior at 400°C. of the resin after normal cure (Fig. 3) and after pyrolysis to 485°C. (Fig. 4), emphasizes the difference between the two structures. The relevant results are presented in Figure 9. The rigidity minimum at ca. 500 min. on oxidation of the normally cured resin at 400°C. very likely corresponds to the minimum at ca. 475°C. in Figure 4 and to the minimum at ca. 150 min. in Figure 7. If this is so, it means that treatment in air at 400°C. of the phosphonitrilic resin leads to a stepwise reaction, in which pyrolysis occurs prior to oxidative degradation. This, too, is apparent from the similar characteristics of the two results of Figure 9 in the later stages of oxidation.

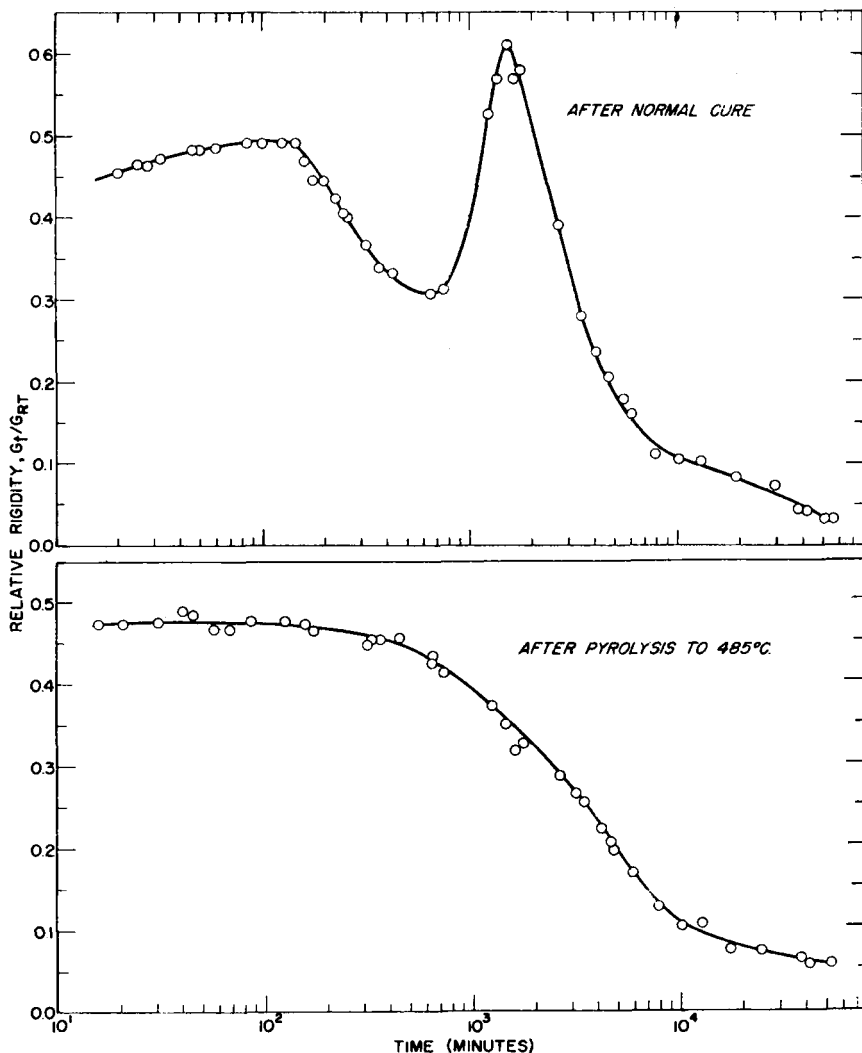


Fig. 9. Isothermal (400°C.) oxidation of phosphonitrilic resin.

CONCLUSION

It has been shown that the torsional braid technique provides a very sensitive tool for following, nondestructively, the liquid-to-solid transformations which accompany the curing of polymers. Curing and thermal softening behavior, as well as pyrolytic and oxidative degradations, are monitored with precision. A successful application of TBA to the study of environmental oxidative degradation implies its utility to studies of other polymeric degradations. Examples might include degradation induced by radiation, and by the vapors of water and organic solvents.

The test of a technique lies in the experimental data. A critical examination of these data will determine, in the course of time, to what extent the possible inherent difficulties which arise from assuming that the supported polymer behaves independently of the substrate, can be overcome. It will be evident that the data which have been obtained to date, have presented self-consistent results, but spurious results are possible. For example, under certain conditions, the polymer sample might undergo dimensional changes due to weight loss, cracking, or shrinkage. Another possible complication is chemical reaction between polymer and support. Such effects may induce false rigidity changes in the system. Hence torsional braid measurements should be carefully monitored and whenever pertinent, additional experimental measurements (e.g., thermogravimetric analysis, differential thermal analysis, electrical resistivity) should be employed.

Instrumentation of the device will permit the monitoring not only of the changes in rigidity, but also the changes in damping characteristics. In addition, the technique should prove to be particularly valuable in the disciplines of inorganic, biochemical, and physiological polymer chemistry. Preliminary results have been obtained on the hardening of an inorganic cement, the denaturation of egg albumin and on the clotting of blood. The complicated nature of these systems limits the use of available analytical and physical methods of organic polymer chemistry. Such experiments will form the basis for future communications.

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Synopsis

Transformations, physical and chemical, which occur in polymeric systems are usually accompanied by changes in rigidity. In the present method, a modified torsional pendulum is employed such that the vertical specimen shaft consists of a fabric braid which is impregnated with the polymeric material under investigation. Therefore, in principle, any changes in the mechanical properties of the composite will be reflected by changes in frequency of free oscillation of the system. This dynamic mechanical technique provides a very sensitive tool for following nondestructively, the liquid to solid transitions accompanying the curing of polymers. In this communication the utility of the torsional braid technique in the study of heat resistant polymers is emphasized. Curing and thermal softening behavior, as well as pyrolytic and oxidative degradations are monitored with

precision. A comparative study between three thermosetting resins, i.e., a phenolic, an unsaturated polyester and a phosphonitrilic, is presented.

Résumé

Les transformations physiques et chimiques, qui ont lieu dans les systèmes polymériques s'accompagnent d'habitude de changements dans la rigidité. Dans la présente méthode on emploie un pendule torsionnel modifié dans lequel l'axe vertical du spécimen consiste d'une tresse de tissus qui est imprégnée du matériel polymérique étudié. Par conséquent, en principe, des changements quelconques dans les propriétés mécaniques du système composite seront reflétées par des changements dans la fréquence de l'oscillation libre du système. Cette technique mécanique dynamique fournit un outil très sensible pour suivre de façon non-destructive, les transitions liquide-solide qui accompagnent la vulcanisation des polymères. Dans cette communication on envisage l'utilité de la technique de la tresse tordue dans l'étude des polymères résistants à la chaleur. Le comportement lors de la vulcanisation et de l'amollissement thermique de même que les dégradations pyrolytiques et par oxydation sont examinées avec précision. On présente une étude comparative entre trois résines thermodurcissables: une résine phénolique, phospho-nitrilique et un polyester non-saturé.

Zusammenfassung

Chemische und physikalische Umwandlungen, die in polymeren Systemen auftreten werden gewöhnlich von einer Änderung der Starrheit begleitet. Bei der hier beschriebenen Methode wird ein modifiziertes Torsionspendel in der Weise verwendet, dass der vertikale Probenschaft aus einem mit dem untersuchten Polymeren imprägnierten Gewebegeflecht besteht. Im Prinzip wird sich daher jede Änderung der mechanischen Eigenschaften in einer Änderung der freien Oszillationsfrequenz des Systems äussern. Dieses dynamisch-mechanische Verfahren bildet ein sehr empfindliches Mittel zur zerstörungsfreien Untersuchung der bei der Härtung von Polymeren auftretenden Flüssig-Fest-Umwandlungen. In der vorliegenden Mitteilung wird die Verwendbarkeit des Torsionsgeflechtsverfahrens zur Untersuchung hitzebeständiger Polymer besonders berücksichtigt. Härtungs- und Wärmeerweichungsverhalten, sowie pyrolytischer und oxydativer Abbau werden genau registriert. Eine vergleichende Untersuchung dreier wärmehärtender Harze, nämlich eines Phenolharzes, eines ungesättigten Polyesters und eines Phosphonitrilharzes, wird durchgeführt.

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