JOURNAL OF APPLIED POLYMER SCIENCE VOL. 8, PP. 489-501 (1964)

Study of Polymers Applicable to Insulation Systems

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Synopsis

In recent years thermosetting polymeric systems have been used extensively as binders in electrical insulation and composite plastic structures with excellent success. However, such properties as post-cure gassing, thermal stability, and high temperature bond strength have always been stumbling blocks for the insulation engineer. Experience has shown that these properties can ultimately affect the dielectric endurance of an insulation when subjected to high voltage stresses. The above-mentioned problems are generally controlled by the organic binders present in the insulation. Test methods have been developed whereby the behavior of the polymers under certain conditions can be predicted, thus increasing the effectiveness of the design engineer.

INTRODUCTION

During the past decade many new dielectric materials have been introduced in the electrical industry. Of particular importance in the insulation of electrical machinery has been the development of systems using thermosetting polymers such as epoxy, polyester, phenolic, and silicone resins. For most insulation applications, such as potting, encapsulation, molding, and high voltage insulation, these polymers have been found to be superior to the thermoplastic types, principally because of their greater thermal stability and retention of physical properties at elevated temperatures.

Some of the basic properties desired in a polymer to be used in the insulation of rotating electrical equipment are as follows: (*1*) good dielectric properties; (*2*) good thermal stability; (*3*) low gassing; (*4*) good mechanical strength; (*5*) ability to withstand long time application of voltage stress.

Other properties of a more practical nature are low toxicity, good processability, compatibility with other materials, and low cost. In this paper, however, emphasis will be placed upon the evaluation of some aspects of properties (*2*) and (*3*) above, i.e., thermal stability and the post-cure gassing at elevated temperatures.

Thermal stability and rate of gassing of cured systems mean different things to various people. For a manufacturer of laminated products, it probably will involve "mold breathing" during the processing. For a molder of structural plastics, it will mean a product with poor physical properties. In both instances, the amounts of gases are large and consequently can be readily detected. Accordingly, process modifications can be made to alleviate such conditions. In the case of relatively sealed dielectric structures when the rate of gas evolution is very slow, the problem is even more complicated. In such cases, a dielectric system will seem to exhibit normal properties. However, during use under applied voltage and thermal stress, the poor thermal stability of the binder may result in chemical changes. This may lead to loss of cohesion and adhesion and consequent loss of bond strength leading to delamination. Concurrent gas evolution may aid the delamination process by aiding the formation of pockets at phase boundaries within such a dielectric structure. In high voltage applications, ionization of the gas in such pockets may well lead to electrical leakage, local heating, tracking, carbon deposits, and finally breakdown of the insulation system. Any boundary such as that between conductor and insulation, or between various layers in the insulation system itself, may suffer from this condition.

One way to obtain better thermal stability is to select a polymer system with appropriate chemical properties. For example, the system should be chemically homogeneous with side reactions eliminated as much as possible.

The purpose of this work was to develop and apply methods for the direct and accurate determination of the thermal stability and gas evolution characteristics at elevated temperatures of fully cured polymeric systems. To this end, use was made of the Chevenard thermobalance to furnish data on the thermal stability of various polymers. An apparatus was constructed to measure the amount of gas evolved at elevated temperatures. The method of applying these tests and the results obtained are discussed below.

THERMAL STABILITY TEST

The thermal stability tests were carried out on the Chevenard thermobalance. Since this instrument is described in detail elsewhere,[1] it will be mentioned only briefly here (Fig. 1). The heart of the balance is a sensitive balance arm, one end of which supports the sample to be tested inside a temperature-controlled furnace. The other end of the balance arm activates the pen of a continuous recorder. As the sample is slowly heated (150°C./hr. is the usual rate), its weight is recorded against time on the recorder chart. At appropriate intervals, the temperature at the sample may be determined by a thermocouple inserted into the furnace and marked along the time axis on the recorder chart. Thus a recording of the sample weight versus temperature is obtained, from which the weight loss of the insulation sample at any desired temperature may be determined. Measurements may also be made of weight loss at constant temperature when desired.

A typical curve obtained with this apparatus is shown in Figure 2. The polymer evaluated in this case was a polyvinyl ethyl ether. The temperature rate of rise was set at 2.5°C./min. The curve itself is self-explanatory

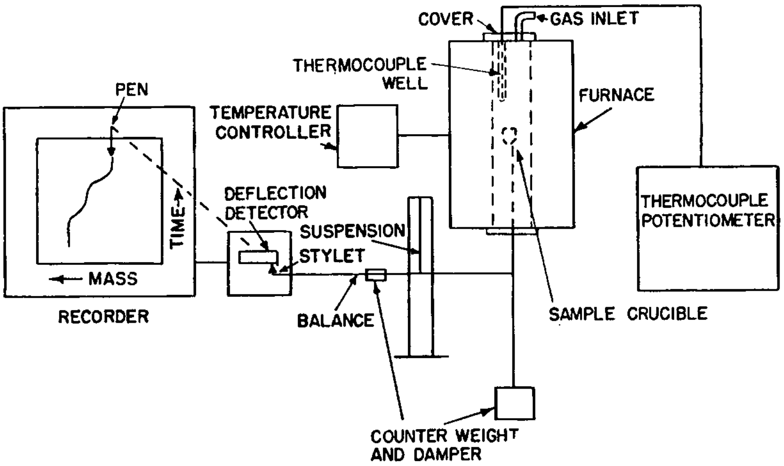

Fig. 1. Functional diagram of Chevenard thermobalance.

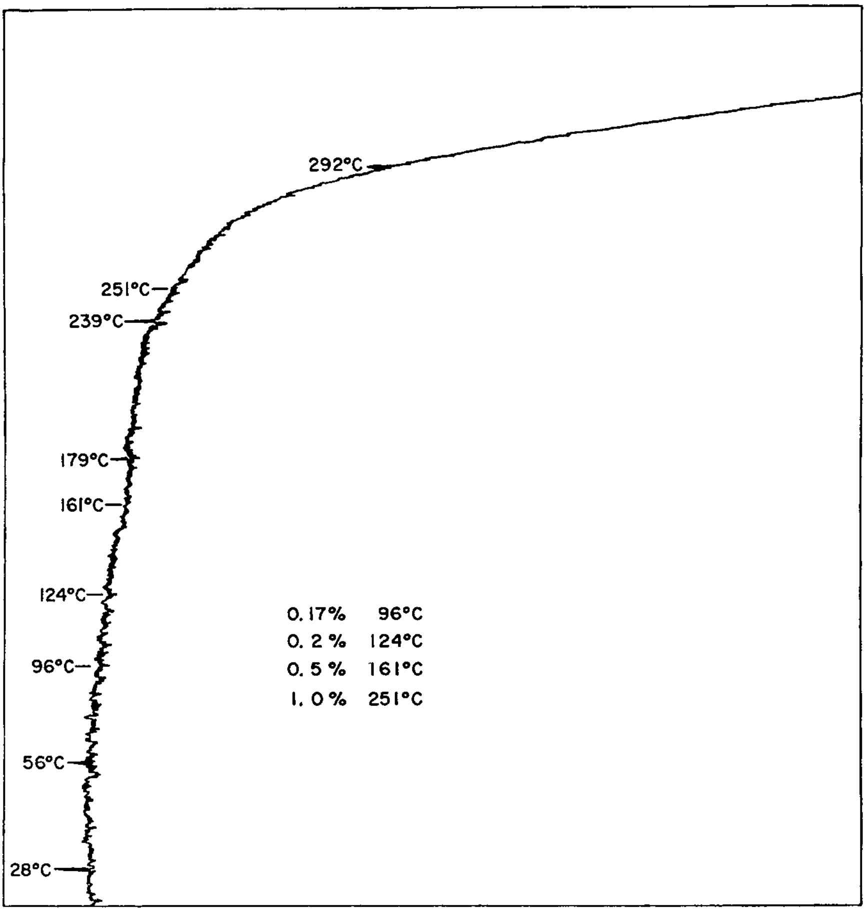

Fig. 2. Thermal stability of polyvinyl ethyl ether.

and the weight loss can be found at various temperature levels on the strip chart.

In determining the thermal stability of the polymers, two series of tests were conducted: short-time tests and weight loss at constant temperature. The results obtained for various resin systems are described below.

a. Short-Time Tests

In this test, the temperature of the oven is raised rapidly at a constant rate of temperature rise. The weight loss of the polymer is recorded on the strip chart and can be readily determined at various temperature ranges. Also, from the same chart, it is possible to deduce the temperature at which various polymers will start to degrade, by exhibiting the first detectible amount of weight loss. On a fully cured system this amount of weight loss can be used as an indication of its relative stability. The tests were conducted under the following conditions: temperature rise rate, 2.5°C./min.; initial weight of fully cured sample, 0.6–0.65 g.; particle size, $^1/_{16}$–$^1/_8$ in.; temperature range, 25–300°C.; samples heated under atmospheric conditions.

The polymers which were used during our studies are those with some adaptability to insulation processes. These resin systems are well known in the industry and some are described in Table I.

TABLE I

Resin	Type	Hardener	Resin/ hardener ratio
Epoxy	Bisphenol A	Diethylenetriamine	100/8
Epoxy	Bisphenol A	Methylene dianiline	100/26
Epoxy	Novolac	BF_3–monoethylamine complex	100/3.5
Unsaturated polyester	Diallyl phthalate	Benzoyl peroxide	100/1.5
Butvar phenolic			
Silicones	Polydimethylsiloxane	Benzoyl peroxide	100/1

In Figure 3 is compiled on a chart the thermal behavior of these resin systems. As indicated, up to 100°C. most of the examined polymers were of the same order of stability, but above that temperature level those with poor thermal stability exhibited appreciably greater weight loss. For instance, some of the investigated epoxies exhibited less than 1% weight loss at 300°C. The values were up to 6% for asphaltic and 5% for vinyl ethyl ether polymers.

Although the temperature conditions are slightly unrealistic, a similar pattern was obtained in weight loss during additional tests at lower tem-

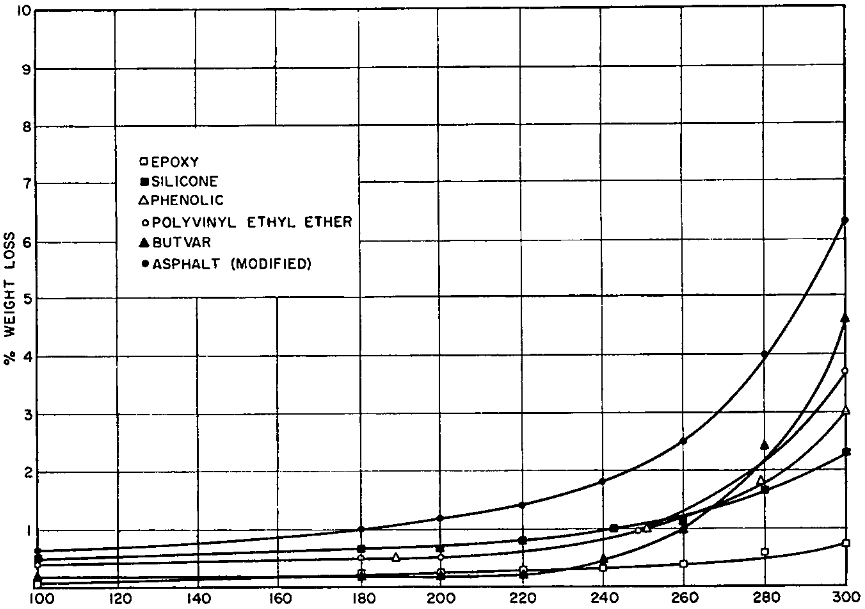

Fig. 3. Thermal resistance of various polymers.

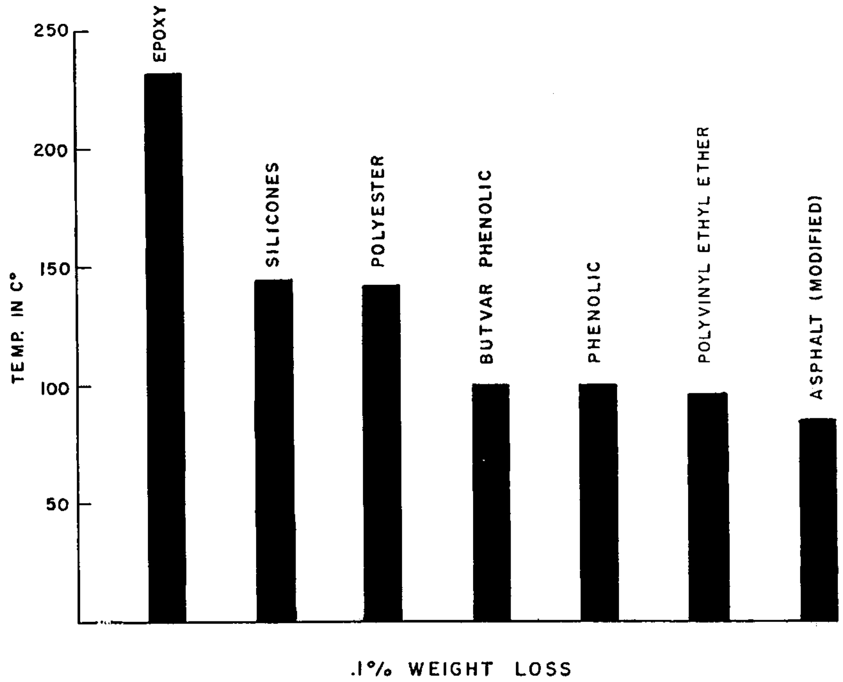

Fig. 4. 0.1% weight loss of various polymers.

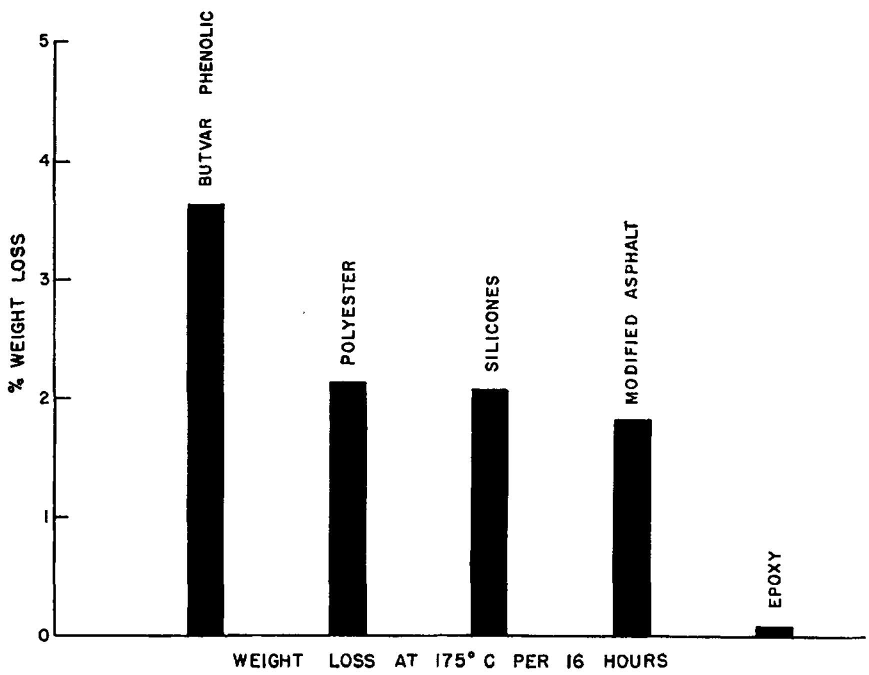

FIG. # 5

Fig. 5. Weight loss at 175°C. for 16 hr. for various polymers.

peratures with exactly the same polymers. Only this time, the check point is the critical temperature at which 0.1% weight loss is detected. These points were picked up from the same chart, and the results were plotted in Figure 4. It can be seen from these data that for the phenolics, vinyl ethyl ether, and asphaltic systems this critical temperature was in the range of 100°C., while for the epoxies it was in the range of 250°C. In between are found silicone, general-purpose unsaturated polyesters, and alkyds.

b. Weight Loss at Constant Temperature

In this test, the oven temperature is brought up to a certain level as quickly as possible and held for a given period. The total weight loss of the specimen is recorded on the strip chart in relationship to the temperature. By actually touching the surface of the test sample with a thermocouple, it is possible to follow its temperature with great accuracy. In Figure 5 is shown the per cent weight loss of various fully cured polymers exposed at 175°C. for 16 hr. under normal atmospheric conditions. From these data, it can be seen that the epoxides exhibited greater stability than the other polymers. For instance, whereas for the epoxies hardly any weight loss was noticed, Butvar phenolic lost up to 4%. The silicones, polyesters, and modified asphalt systems exhibited close to 2% weight loss under similar test conditions.

POST-CURE GASSING

Standard tests, such as weight loss determination after aging or oven baking, are good indications of the behavior of polymers under thermal stresses. It was found necessary, however, to supplement the thermal behavior of polymers with its post-cure gassing properties. Since the amount of gassing referred to is quantitatively very minute, for obvious reasons the studies had to be conducted under some accelerating means. A vacuum/heat combination appeared to provide a reasonably practical means for gas evolution investigations. The gassing in question, caused primarily by factors such as adsorption, thermal sensitivity, and residual light fractions, is important for insulation processes such as potting, high voltage structures, and other sealed applications. This is more so where the insulation structures consist of relatively nondiffusing thermoset structures.

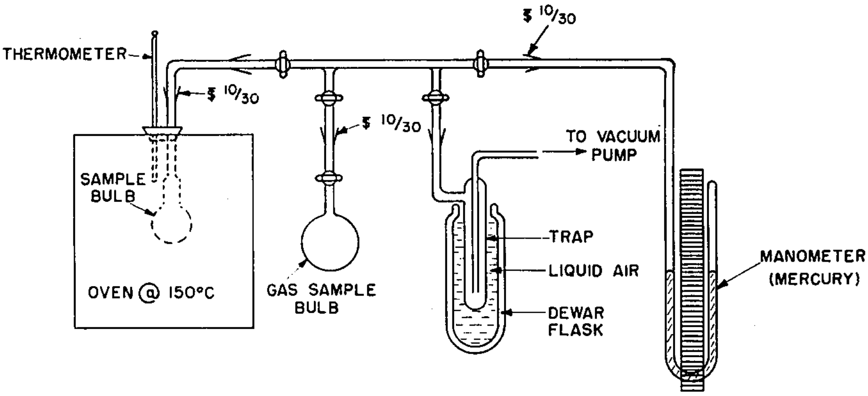

Fig. 6. Diagram of gas evolution apparatus.

The apparatus designed for the gassing studies is shown in Figure 6. It consists of a 100-mm. single container located in an air circulating oven. The sample to be analyzed is placed in this container. Glass tubing with ground glass joints and vacuum stopcocks are used throughout to make the system vacuum tight. The container is connected to a high capacity vacuum pump. In between, a gas sample bulb of about 300-ml. capacity was placed and used to collect the gases during and after the vacuum heat treatment of the polymer. The pump was protected by a liquid nitrogen trap. The manometer was of a closed-end mercury type. The oven could be controlled automatically to maintain the temperature at 150°C.

a. Calculations

The pressure at any time, as read on the mercury manometer, is easily converted to the volume of gas evolved per gram of sample, reduced to room temperature (25°C.), by application of the ideal gas laws. The volume of the apparatus must be known and is determined by calculation or by

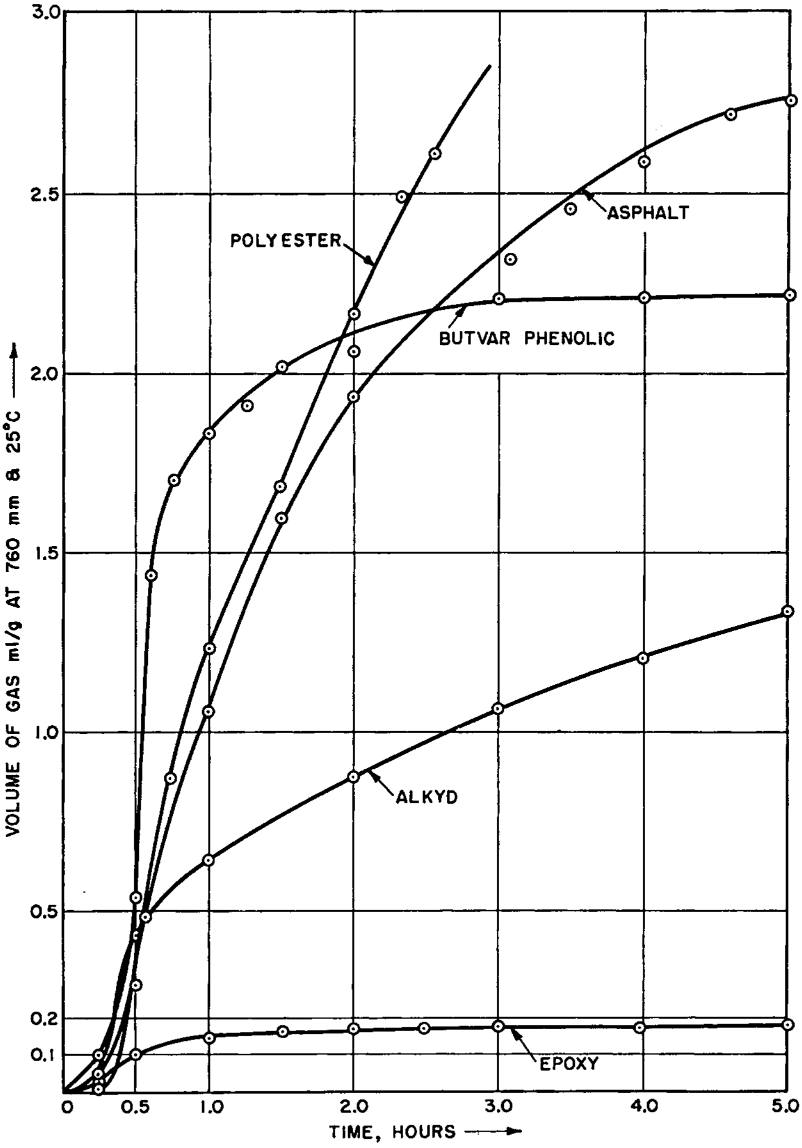

Fig. 7. Gas evolution at 150°C. for various polymers.

measuring the volume of water a given section contains. Then the following eq. (1) applies:

$$P(0.70\ V_s + V_t)/760W_s = V_2 \qquad (1)$$

where P is the pressure as read at manometer (in millimeters of mercury), V_s is the volume of the sample bulb in oven (in milliliters), V_t is the volume of the connecting tubing at room temperature (in milliliters), W_s is the weight of sample (in grams), V_2 is the volume of gas produced per gram of sample reduced to 760 mm. and 25°C.; $0.70 = T_{25°C.}/T_{150°C.} = 298°K./423°K.$

b. Experimental

The gas evolution studies were conducted under the following conditions. A 10–20 g. sample of finely divided cured polymer was heated under vacuum for 7 hr. at 100°C. This post-cure baking was found necessary in order to completely post-cure the material. At this point, the system was closed off to the vacuum pump and the temperature of the oven readjusted to 150°C. If the polymer had any tendency to gas, volatiles evolved from the sample. Pressure built up continuously on the mercury manometer, from which the rate of gas evolution could be calculated. The gas pressure, controlled by the initial weight of the specimen, is maintained below the critical pressure range to eliminate pressure drop due to condensation.

Figure 7 shows some of the results of the investigations. As mentioned above, the polymeric systems were fully cured prior to testing. The particular epoxy polymers tested exhibited the lowest post-cure gassing properties. Surprisingly, however, the polyesters generally accepted as nongassing systems showed rather comparatively high gas evolution characteristics. In a cycle of 5 hr. the epoxies evolved less than 0.2 ml., the polyesters over 2.5 ml. within 3 hr., while the phenolics and alkyds were in between (about 1.5 ml. in 3 hr.).

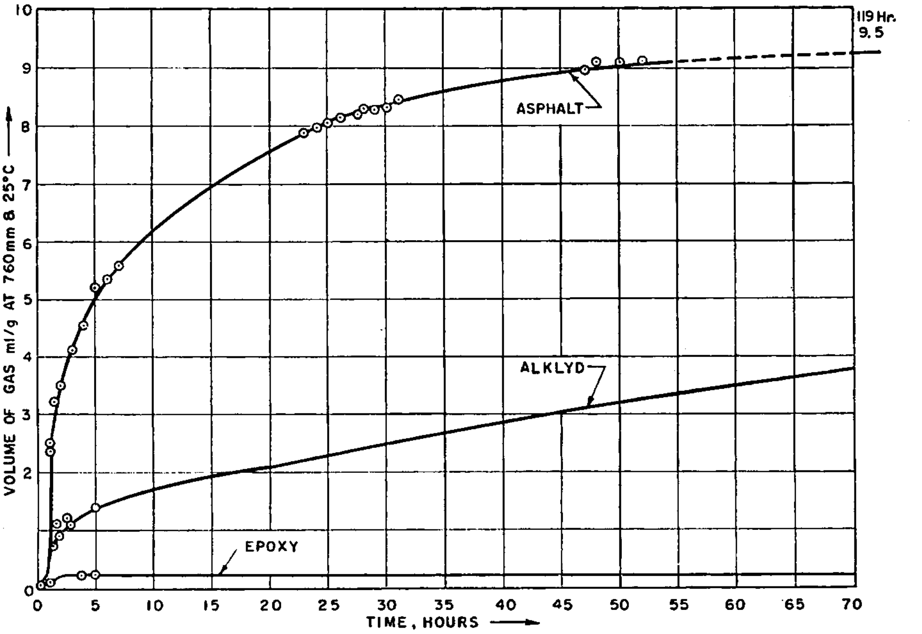

Fig. 8. Gas evolution at 150°C. at extended vacuum cycles.

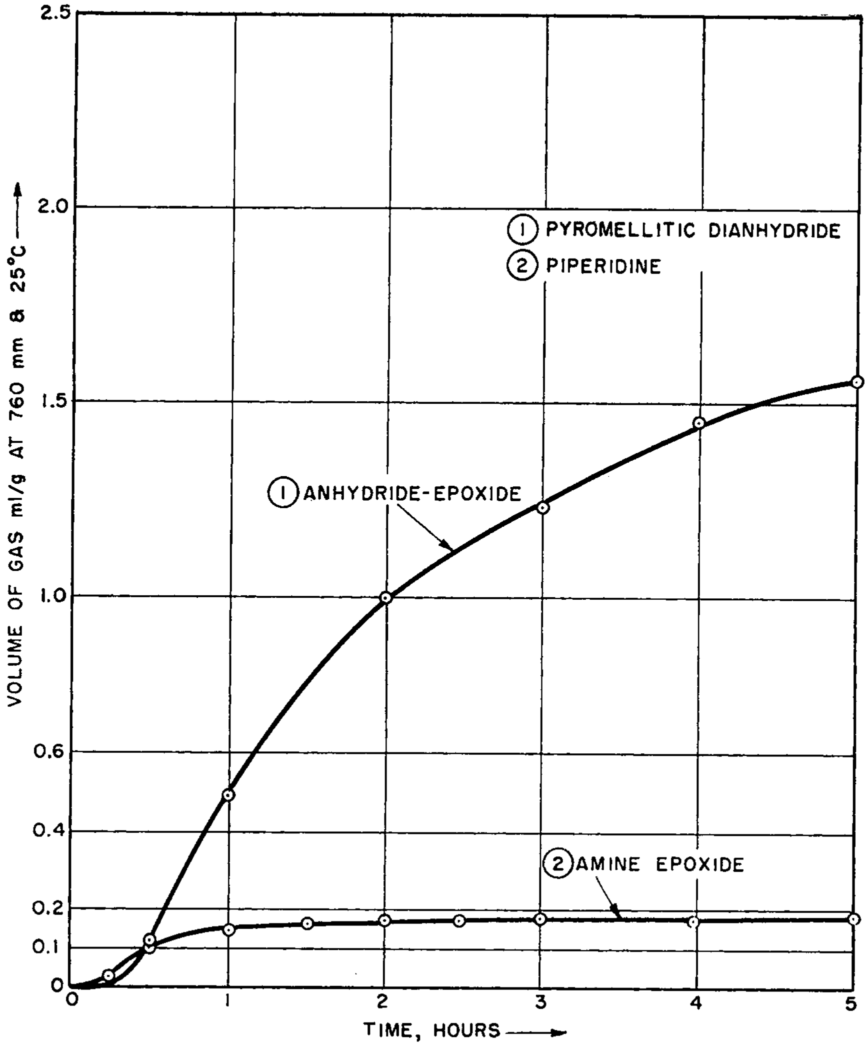

Fig. 9. Gas evolution curves at 150°C. for anhydride-cured epoxide vs. amine-cured epoxide.

From these data it can be seen that not all thermoset polymers exhibit the same gassing characteristics under similar conditions. From a practical standpoint for many applications, this phenomenon would not be a major problem if within a reasonably short period the gassing curve would show some flattening. For this reason, in another series of tests the vacuum cycle was extended over 50 hr. During these tests (for which results are shown in Fig. 8), the epoxy polymers indicated a stabilized pressure within 4–5 hr., whereas the polymers with higher gassing tendencies continued to evolve volatiles. Also, the accumulation of volatiles during this cycle was found to be a great deal more than a sealed structure can tolerate.

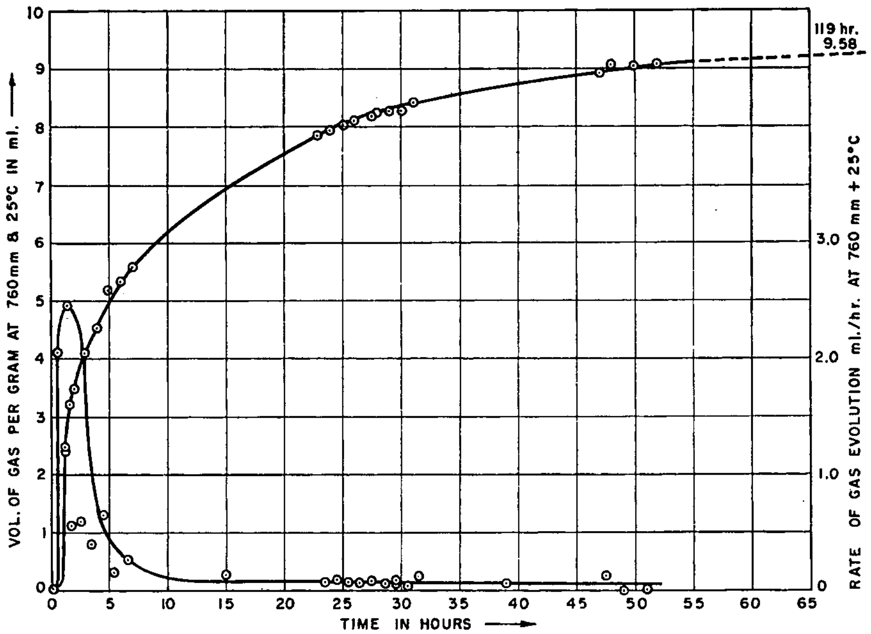

Fig. 10. Gas evolution at 150°C. of modified asphalt.

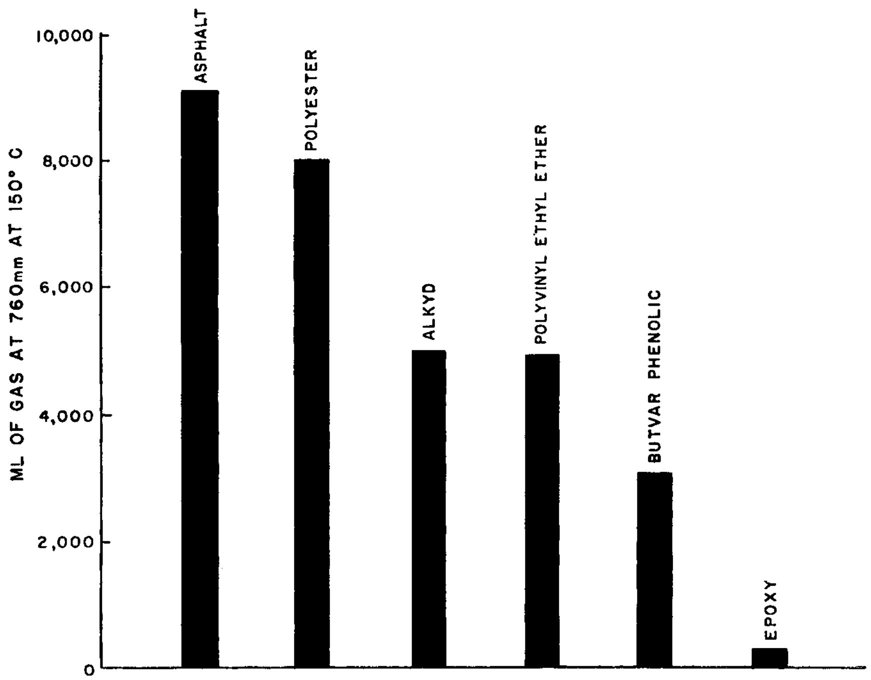

Fig. 11. Volatiles evolution from 1000 g. of polymer.

Epoxies evolved less than 0.5 ml., as compared with 9 ml. for asphalt and polyester and up to 4 ml. for alkyds.

In addition to differences among types of polymers, it was found that particular curing mechanisms may, to a certain degree, influence post-cure gassing properties within the epoxy family itself. In Figure 9 the volatile evolution of amino-cured (piperidine) epoxides versus anhydride-cured (pyromellitic dianhydride) epoxides is shown. For the systems tested, the anhydride-cured epoxy gave off seven times as much volatiles as the amine-cured type. It is possible that similar phenomena might be expected within other polymer families.

In Figure 10 is plotted the total amount of gases evolved during 120 hr. versus the rate of gas evolution in the same period. The material investigated in this case was an oil-modified asphalt. These tests were conducted after relative degassing of the specimen. As shown in the figure, the rate of gas evolution in the beginning is high, going from a 2.5 ml. peak during the first 2 hr. then rapidly diminishing. However, it is interesting to point out that, with this particular system, during the last 40 hr. the rate of gas evolution is almost constant in the range of 0.2 ml./hr.

Figure 11 summarizes the total amount of gases expected under these conditions from 1000 g. of given polymer. As indicated, volatile evolution from the epoxies, particularly the amine-cured epoxides, is less than one tenth as much as that from the other polymers tested. The materials evaluated where those which appeared to be especially adaptable to electrical insulation processes.

CONCLUSION

In the search for the right polymer and the right process for dielectric applications, many tests are available. They all contribute toward the process of material selection. Very often the design engineer is confused by the wide choice of existing polymeric systems. Undoubtedly, environmental tests will be the final criterion on the performance of a specific dielectric structure. Unfortunately, such tests are time consuming and sometimes exhorbitant in cost.

The tests described in this paper were found useful in the preliminary screening work of such polymers. Furthermore, these tests, based on the thermobalance and gas evolution may be readily adapted to routine searching and testing techniques. They can provide the technical searcher a better screening and understanding of the behavior and capability of organic binders for specific dielectric applications.

Reference

1. *Operating Handbook, Chevnard Thermobalance,* R. V. Ferner Co., Inc., Malden, Mass.

Résumé

On a beaucoup employé ces dernières années avec succès des systèmes polymériques thermodurcissables comme liants dans les isolants électriques et comme structures plastiques mixtes. Cependant, les propriétés telles que le gonflement après traitement, la stabilité thermique et la force des liens à haute température des isolants ont toujours constitué des difficultés considérables pour l'ingénieur chargé de l'isolement. On a montré expérimentalement que ces propriétés peuvent affecter de façon prépondérante l'endurance diélectrique d'un isolant soumis à de hauts voltages. On controle généralement les problèmes mentionnés ci-dessus en incorporant des liants organiques dans l'isolant. On a mis au point des méthodes de vérification grâce auxquelles on peut prévoir le comportement de polymères sous certaines conditions, augmentant ainsi l'efficacité du travail de l'ingénieur.

Zusammenfassung

In den letzten Jahren wurden wärmehärtende Polymersysteme in grossem Masse als Bindemittel bei elektrischen Isolierungen und zusammengesetzten Kunststoffstrukturen mit bestem Erfolg benützt. Eigenschaften wie Gasbildung bei der Nachhärtung, Wärmebeständigkeit und Verbindungsfestigkeit bei hoher Temperatur bildeten jedoch immer Schwierigkeiten für den Isolierungsingenieur. Die Erfahrung hat gezeigt, dass diese Eigenschaften letztlich die dielektrische Beständigkeit einer Isolierung bei Hochvoltbeanspruchung beeinflussen können. Die oben erwähnten Probleme werden im allgemeinen durch das in der Isolierung enthaltene organische Bindemittel bestimmt. Es wurden Testmethoden entwickelt, die eine Voraussage des Verhaltens von Polymeren unter gewissen Bedingungen gestatten und so die Arbeit des Konstruktionsingenieurs wirksamer machen.

Received November 1, 1962