

The Effect of Nickel Incorporation on Some Physical Properties of Epoxy Resin

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Abstract—The J-E characteristics of samples of epoxy resins mixed with nickel powder in different concentrations have been tested and a log-log straight line behaviour in both the low- and high field regions is observed. Ni-concentration has significant influence on the calculated constants of the J-E relationship. The d.c. electrical resistivity (ρ) of the samples are measured from the room temperature up to about 400 K. The variation of ρ with T obeys the exponential relation of ordinary dielectrics in three temperature regions. The parameters characterizing the ρ - T dependence change considerably with Ni-concentration. Due to the existence of nickel in different concentration a "true" compensation effect is observed with three characteristic compensation temperatures. The mechanical hardness of the samples was investigated as a function of Ni-concentration.

Keywords—Epoxy resin, J-E characteristics, Electrical resistivity, Mechanical hardness.

I. INTRODUCTION

Because of their strength versatility and excellent adhesion to a variety of surfaces, epoxy resin adhesives have revolutionized joining and fastening technology in some industries such as various military aircrafts and space vehicles components in which weld bonding process has been evaluated and in automotive industry. In all of these applications, to establish a reliable manufacturing process, the adhesive properties should be significant. Time control and temperature; greatly influence the surface characteristics which in turn affect the processing factors [1]. Niazi et. al. [2] reported that the addition of aluminum and bronze to epoxy resin increased shear strength with curing temperature in the whole range up to 125 °C. The interparticle distance is of vital importance on determining the strength of the particular composite, being maximum when it is dispersed as finely as possible (in the order of several microns [3]) as for graphite powder.

The properties of cured epoxy resins may be varied over a wide range according to both the curing agent and curing cycle. Also, incorporating fillers into the uncured system changed considerably these properties [3-7]. Fillers may be added to epoxy resins to reduce cost, lower the coefficient

of thermal expansion, reduce shrinkage, increase thermal conductivity, alter surface hardness, reduce exotherms, improve adhesive properties and/or change the handling characteristics of the resin system to import the desired flow or thixotropic properties. One of the main characteristics of epoxy resins is the possibility of enhancing their properties by varying the temperature of performance by curing [4, 8, 9].

Epoxy-based adhesives film were prepared using conductive fillers of different size, shape, and types, including Ni powder, flakes, and filaments, Ag powder, and Cu powder [10]. In all cases, the obtained results of conductive filler addition, the planar resistivity levels for the composite adhesive films increased when the film thickness was reduced. In the other hand a newly developed strategy offering promising results is to reinforce epoxy matrices with nano-sized organic and inorganic particles such as carbon nanotubes (CNTs), carbon nanofibres (CNFs), nanoclays, metal oxide nanoparticles, etc. and make new materials with enhanced properties [11-15]. Also Graphene can significantly improve physical properties of epoxy at extremely small loading when incorporated appropriately. The structure, preparation and properties of epoxy/graphene nanocomposites are reported [16]. This work has been focused on the processing methods and mechanical, electrical, and thermal properties of the nanocomposites [16].

The interrelations between different properties, whether electrical, thermal, mechanical or others, of the components of such heterogeneous materials become more difficult and necessitate deep research in solid state physics because it was found that the volume fraction calculations are efficient as long as the properties of the individual components are near to one another and the components themselves are regularly distributed [17,18], otherwise the percolation theory may apply [18].

In this article the J-E characteristics, d.c. electrical resistivity and mechanical hardness of epoxy resin filled with Ni powder will be given as a function of temperature and nickel concentration.

II. EXPERIMENTAL WORK

2.1. MATERIALS

- a) Adhesive: Two pots of epoxy resins were used. Their characteristics are as follows:
- i- Composition:
 Resin: Bisphenol-A Epichlorohydrine, molecular weight <700 (Araldit AW 106, CIBA-GEIGY B.V. Switzerland Reaction Product)
 Hardener: Triethylene tetramine
 - ii- Mix ratio: 1 : 0.8 (by weight) Resin to Hardener.
 - iii- Pot life: 20 minutes at room temperature.
 - iv- Cure cycle 24-48 hours at room temperature.
- b) Filler: Nickel powder in the following concentrations: 5, 10, 15, 20, 30 and 40 % by weight.

2.2. SAMPLES

Samples for the present investigation were prepared in the form of thin slabs with surface area of about 0.9 x 0.7 cm² and their thickness was 0.13 cm. Conducting silver paste was painted on the two opposite areas to serve as electrical contacts. Home designed holder was used for mounting the studied samples.

2.3. Measuring PROCEDURE

The electrical resistivity and the current-voltage characteristics were measured using Keithley electrometer type 610C. The error in the measured values is less than 3%. The sample temperature was measured and controlled by means of a copper-constantan thermocouple with the accuracy of 0.1 K. All the measurements were taken under rough vacuum of about 10⁻³ Torr.

III. RESULTS AND DISCUSSIONS

3.1. THE J-E CHARACTERISTICS

The J-E characteristics (where J is the current density and E is the applied d.c. electric field intensity) of the samples under investigation are shown in Fig. (1). The dependence on nickel concentration is evident. As a general, the J-E dependence on a log-log scale is two straight lines one in the low-field (LF) and the other in the high-field (HF) regions. The equation of the straight lines has, in general, the form:

$$J = A E^s \quad (1)$$

Where s is an exponent and A is a constant having the nature of conductivity. The values of A and s strongly depend on both nickel concentration and value of the applied electric field.

It is clear that two straight lines characterize the J-E dependence in Fig. (1).

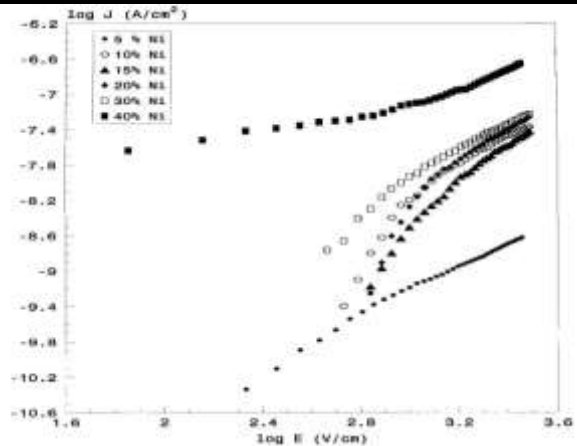


Fig. 1: J-E characteristics of epoxy resins samples incorporated with different concentrations of nickel powder.

This behaviour may be explained on the basis of the double injection model proposed by Kao [19] For the Ag-resin-Ag sandwich, Ag electrode can be considered as nearly ohmic contact in case of tunneling electron injection and as nearly blocking contact in case of hole injection. So, in the low-field bulk-limited regime a single injection is mainly existed. Most of the injected electrons cover short distance before they are trapped. The excess electrons form a negative space charge being highly condensed very close to the electrode. The space charge tends to reduce the rate of electron injection and, on the other hand, tends to enhance the field towards the other electrode. With increasing the applied electric field the injected carrier concentration increases, and hence the density of the space charge, until the external electric field reaches a value at which the space charge becomes high enough to slow down the rate of electron injection. In addition, the space charge tends to move away from this electrode until it reaches a position at which holes start to be injected from the other electrode. The injected holes tend to counteract the effects of the space charge. As a result of the thermal detrapping, a decrease in the density of the space charge could be introduced. The rate by which J increases with increasing E depends upon the resultant of these effects.

As it is clear from Fig. (2), three different behaviours could be distinguished. The first is that of the sample with 5% Ni, the second is that of samples incorporated with 10, 15, 20 and 30% Ni. The last is the behaviour of the sample with 40% Ni. The latter case is the unique for which an ohmic conduction is presented in the HF region. This is clearly due to the high concentration of metallic atoms. The weak J-E dependence in the LF region of this case, which is also unique, is probably attributed to low mobility because of scattering effects. For the other samples (with 10, 15, 20 and 30% Ni), the carrier concentration sharing from the filler increases with increasing E. The increase in E at the beginning cause a high increase in J up to certain

value (denoted by E_0) at which the mobility decreases and consequently the current density decreases.

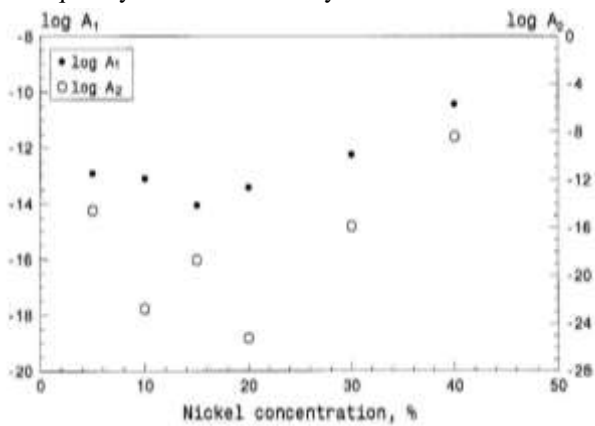


Fig. 2: Dependence of the constant A on nickel concentration in both the low- and high-field regions of epoxy resin samples.

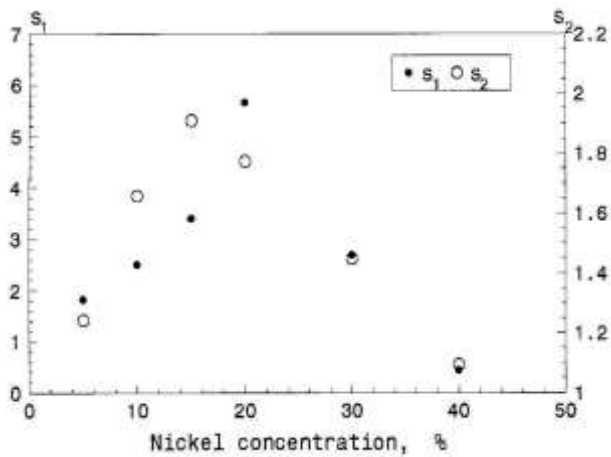


Fig. 3: Dependence of the exponent of equation (1) in the low- and high field regions on nickel concentration of epoxy resins sample.

The dependence on nickel concentration of the exponent s in both the low- and high-field regions and the values of the electric field E_0 at which the regime of conduction changes are shown in Figs. (2&3). Graphical representation of nickel concentration dependence of constant A in both the low- and high field regions is also given in Fig. (4). From the last three figures it is clear that the most effective nickel concentration on the parameters of equation (1) is around 20 %.

The dependence of the ratio H ($H = s_2/s_1$, where s_1 and s_2 are the values of s at the LF and HF regions, respectively) on nickel concentration is shown in Fig. (5). From this figure one can predict that the value of $H=1$ (the effect of the two mechanisms is equal) at nickel concentration equals to 35%.

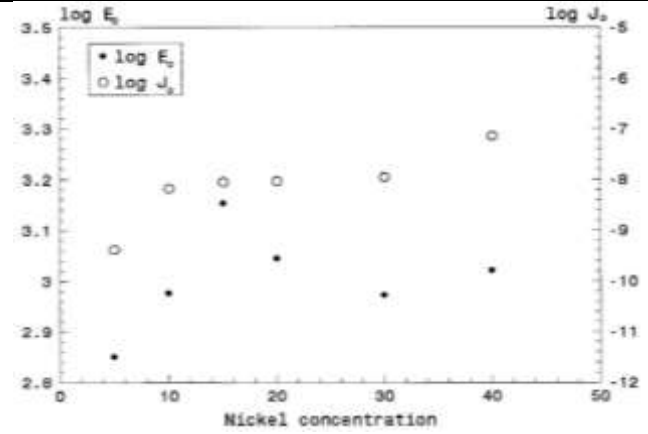


Fig. 4: Dependence of the exponent of equation (1) in the low- and high field regions on nickel concentration of epoxy resins sample.

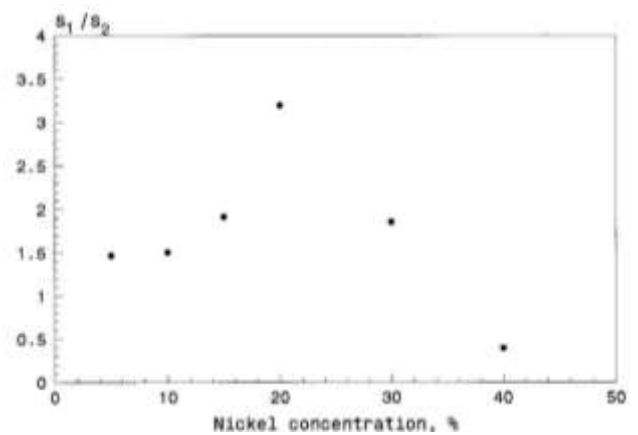


Fig. 5: Nickel concentration dependence of the ratio between the two exponents of equation (1) in the low- and high-field regions of epoxy resins samples.

3.2. D.C. ELECTRICAL RESISTIVITY

The study of the d.c. electrical resistivity ρ of epoxy resins could be divided into two parts. The first part is the effect of nickel concentration on the temperature dependence of ρ while the second part is the compensation effect of the system composed of epoxy resin samples with and without filler used in the present investigation.

3.2.1. FIRST PART

The temperature dependence (up to 350 K) of the electrical resistivity of pure samples of epoxy resins as well as samples incorporated with different concentrations of nickel up to 40% by weight is given in Fig. (6). It is shown, that the relation between ρ and T can be divided into three parts. Each part may be represented by an equation of the form:

$$\rho = \rho_0 \exp. (w/k_B T) \quad (2)$$

Where ρ_0 is the pre-exponential parameter, w is the activation energy of conduction and k_B is Boltzmann's constant.

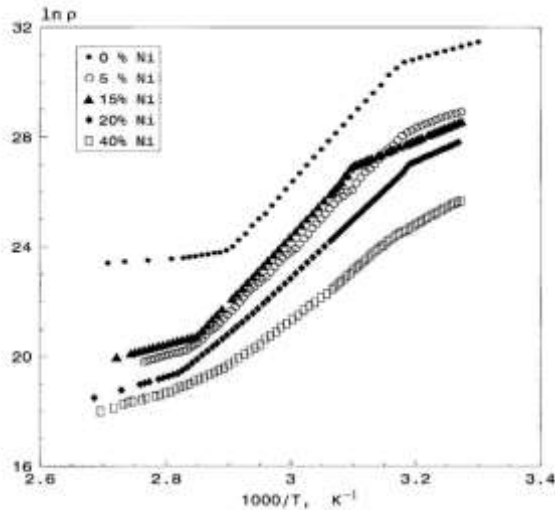


Fig. 6-a: Electrical resistivity of epoxy resins samples incorporated with different concentrations of nickel powder as a function of temperature.

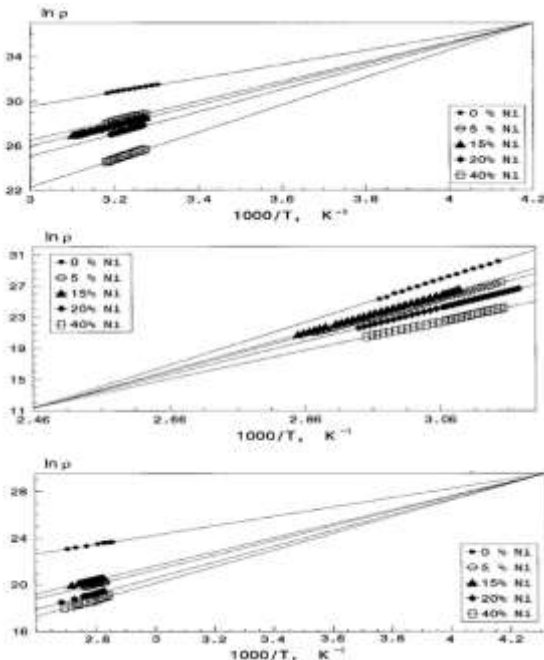


Fig. 6-b: Extrapolation of the straight lines representing ρ-T dependence in three temperature regions of epoxy resins samples incorporated with different concentrations of nickel powder.

The existence of nickel has a strong influence on both the electrical resistivity and its temperature dependence. The value of ρ at room temperature decreases steadily with increasing nickel concentration. The value of the activation energy of conduction deduced from equation (2) varies with nickel concentration (C) having its maximum value of 2.08 eV at C = 15 % in the intermediate temperature range as shown in Fig. (7).

3.2.2. SECOND PART

The so-called compensation effect, proposed by Meyer-Nedel [20-23], describes linear relationship between the logarithm of the pre-exponential factor ρ₀ and the activation energy of conduction w in the form:

$$\ln \rho_0 = \alpha w + \beta \quad (3)$$

Where α and β are two independent constants.

The compensation effect is classified into two types; "apparent" and "true" [23] for both expressions (in Equation 3) is valid. However, in the "apparent" compensation effect, for each particular w-value unique values of ρ₀ and ρ(T) does not exist and the system cannot be precisely defined. On the contrary, in the "true" compensation effect an excellent correlation between ln ρ₀ and w from one hand and between ρ(T) and w from the other hand may be obtained.

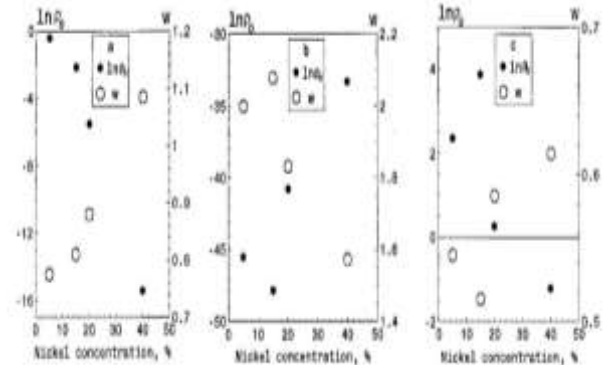


Fig. 7: Nickel concentration dependence of ln ρ and w in the low-, intermediate- and high-temperature ranges for epoxy resins samples filled with Ni-powder.

When compensation phenomena is observed and the Meyer-Nedel rule can be applied, Dewsberry [24] showed that the Arrhenius lines describing the ρ-T relationship when extrapolated must pass through a common point not necessarily on the ρ axis. So, the compensation effect can be expressed mathematically by a three-constant equation of the form:

$$\ln \rho(T) = \ln \rho'_0 - \left(\frac{1}{T_0} + \frac{1}{T} \right) \frac{w}{k} \quad (4)$$

Where T₀ is a characterizing temperature known as the compensation temperature.

This effect is now established experimentally in many organic semiconductors, polymers and various other materials [25-28]. Comparing equations (2), (3) and (4) one can get

$$\text{And } \ln \rho_0 = \ln \rho'_0 + \frac{w}{kT_0} \quad (5)$$

$$\alpha = \frac{1}{kT_0} \quad \& \quad \beta = \ln \rho'_0 \quad (6)$$

hence:

This phenomenon was checked in case of plane samples subjected to thermal recycling and equations (3-6) were found to be successfully applied to this system.

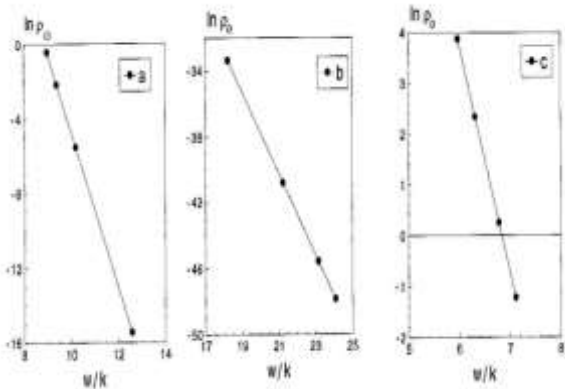


Fig. 8: Relation between $\ln \rho_0$ and w/k_B (k_B is Boltzmann's constant) in the low-, intermediate- and high-temperature ranges for epoxy resins samples filled with nickel in different concentrations.

Equations (3), (4) and (5) are now under test in the present study. Four samples of epoxy resins with different concentrations of nickel in addition to sample free from Ni are now consisting the system for which the validity of equations (3-6) is tested. As it is clear from Fig. (6), the extrapolation of the straight lines representing the ρ -T relationship intersect at single point for each of the three parts of the dependence. The characteristic compensation temperature and the corresponding values of ρ_0 are included in Table (1). At the compensation temperature the values of $\rho(T_0)$ gives the ρ^* values. On the other hand, linear plots of $\ln \rho$ versus w/k could be obtained as expected from equation (3), Figure (8) and Table (1) give the values of T_0 and ρ_0 obtained from different plots. As it is clear from Table (1), the results obtained for $\ln \rho_0$ and T_0 calculated using equations 3 and 4 are consistent with each other.

Table.1: Values of T_0 and ρ_0 for both the low- and high-temperature ranges deduced using equations (3) and (4)

Range	low-temperature region		intermediate-temperature region		high-temperature region	
Equation	$\ln(\rho_0)_1$	$(T_0)_1$, K	$\ln(\rho_0)_2$	$(T_0)_2$, K	$\ln(\rho_0)_3$	$(T_0)_3$, K
(3)	36.77	240±2K	11.64	404±3K	30.47	225±2K
(4)	36.95	239±2K	11.75	403±3K	29.50	229±2K

3.3. MECHANICAL HARDNESS

The mechanical harness of samples of epoxy resins incorporated with different concentrations of Ni was investigated through the calculation of the Brinell Hardness Number (DPH) [29] at room temperature using the relation:

$$DPH = \frac{1.8544 \times L}{d^2} \quad (7)$$

Where L is the load in kg and d is the average diagonal in mm. Fig. (9) shows the dependence on Ni-concentration of the DPH of the samples treated in this investigation. From the figure it is clear that the maximum value of the DPH is 64 kg/m² corresponds to 20 % Ni-concentration.

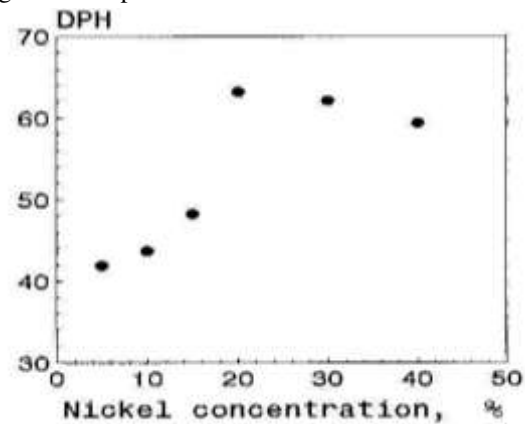


Fig. 9: Nickel concentration dependence of the DPH of epoxy resins samples filled with nickel powder.

IV. CONCLUSION

- Addition of nickel powder with the ratio 35% by weight to plain epoxy resins improved the response of the material to external electric fields in the temperature range 295-370 K.
- Interpretation of conduction in epoxy resins filled with nickel is based on the competition between bulk conduction (increases with increasing nickel concentration) and injection carrier conduction controlled by trapped space charge (trap release increases with temperature).
- A “true” compensation phenomena is observed for a system of samples of epoxy resins filled with different concentrations of nickel powder.
- The existence of three compensation temperatures indicate three characterizing conduction mechanisms in epoxy resins according to the temperature range.
- Addition of nickel powder may replace the effect of high temperature curing since both improve appreciably the electrical conductivity of plain epoxy.

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