



DSC and Dielectric Properties of Epoxy Resin Reinforced with (ZrO₂, CuO) Nanoparticles

Haneen M. Hassan¹, Sabah A. Salman^{2*}

¹Student, Department of Physics, College of Science, University of Diyala, Diyala, Iraq.

²Professor, Department of Physics, College of Science, University of Diyala, Diyala, Iraq.

Abstract

In this research the additive effect of Zirconium Oxide (ZrO₂), Copper oxide (CuO) nanoparticles to epoxy resin as a matrix have been studied, in addition to manufacturing hybrid composites from the same nanoparticles which are (CuO/ZrO₂) to epoxy resin as a matrix too. The hand lay-up method is using to manufacturing the composites from the epoxy resin and the nanoparticles with different weight ratios ((0, 0.3, 0.6, 0.9) wt%), the thermal and dielectric tests have been done of all prepared composites. The effect of the weight ratio of the reinforcement materials on the thermal properties of all-polymer composites has been studied also. The practical results have shown that the differential scanning calorimetric (DSC) test has shown that the glass transition temperature of all-polymer composites increases at all weight ratios of reinforcement materials compared with pure epoxy and the highest value of glass transition temperature is to the composite (EP-ZrO₂) which equal (89.97 °C), also the crystalline melting temperature of all-polymer composites has shown irregular behavior compared with pure epoxy by increasing the weight ratio of reinforcement materials. The effect of the weight ratio of the reinforcement materials on the dielectric properties of all-polymer composites have been studied, the practical results have shown a decrease in dielectric constant with increase the frequency for all weight ratios of reinforcement materials, and also increasing the dielectric constant with increasing the weight ratio of the reinforcement materials at the same frequency.

Paper Status

Received : Dec 2020
Accepted : Feb 2021
Published : Mar 2021

Key Words

Epoxy resin,
Dielectric properties,
Differential scanning calorimetry,
Nanoparticles,
Polymer composites,

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Citation: Haneen M. Hassan, Sabah A. Salman. "DSC and Dielectric Properties of Epoxy Resin Reinforced with (ZrO₂, CuO) Nanoparticles" International Research Journal of Science and Technology, 2 (2), 379-383, 2021.

1. Introduction

Polymers became an essential and ubiquitous part of our lives: clothing, car parts, aircraft frames, telephones, computers, human body prostheses, and numerous other material goods that we take for granted are composed largely of polymers [1]. The main goal in the majority of the research in polymer science, or general materials science, since the beginning of the (20th) century can be summarized as the quest for structure-property relationships. As the development of new chemistries to obtain new materials is very long and arduous,

polymers are often blended to obtain non-linear or synergic material properties [2].

Polymer materials are made in different varieties; the polymer blends are classified as one of those varieties. Two or more existing polymers may be blended for various reasons. One reason is to achieve a material that has a combination of the properties of the constituents, e.g. a blend of two polymers, one of which is chemically resistant and the other tough. Another reason is to save costs by blending a high-performance polymer with a cheaper material. A very important use of the blending is the combination of an elastomer with a rigid polymer to reduce the brittleness of the rigid polymer [3].

Polymer composites due to their lightweight, chemical and corrosion resistance as well as heterogeneous

* Corresponding Author: Sabah A. Salman
Department of Physics, College of Science, University of
Diyala, Diyala, Iraq.
Email: pro.dr_sabahanwer@yahoo.com

composition provide unlimited possibilities of deriving any characteristic material behavior. This unique flexibility in design tailoring and other characteristics, such as ease of manufacturing, high specific strength, stiffness, shape molding, corrosion resistance, durability, adaptability, and cost-effectiveness, have attracted the attention of engineers and material scientists, and technologists. They had become materials of (21st) century to meet the requirement of space, missile, marine, and medical aid technologies [4].

2. Materials and Methods

2.1 Materials Used

Matrix: Epoxy polymer matrix is prepared by mixing [3:1] parts by volume of epoxy resin (Nitofill, EPLV with hardener (amine) supplied by a company Fosroc Jordan. Epoxy resin contains epoxide groups that serve as cross-linking points. The resin reacts with the hardener to form long chains of cross-linked polymer.

Fillers: In this paper, two types of nanomaterials were used to prepare composites and hybrid composites (ZrO₂ with particle size (40-50 nm) supplied by a company Hongwu Nanometer of purity (99.9%), CuO with particle size (50 nm) supplied by a company US Research Nanomaterials, Inc. of purity (99.5%)), with weight ratios (0.3, 0.6, 0.9 wt%).

2.2 Experimental Details

The nanoparticles (Zirconium Oxide (ZrO₂), Copper Oxide (CuO)) are weighted according to equations below and added to the epoxy resin firstly with different weight ratios ((0.3, 0.6, 0.9) wt%), this step was happened in the hood to reduce the interaction between nanoparticles and air to reduce the pollution with the environment this is because of this interaction increase the agglomeration of the nanoparticles and decrease the polymer matrix chain of nanoparticles with epoxy.

$$W_p(\%) = \frac{w_p}{w_c} \times 100 \dots \dots \dots (1)$$

$$W_m(\%) = \frac{w_m}{w_c} \times 100 \dots \dots \dots (2)$$

Where:

W_p, W_m - weight fraction of the reinforcement material and matrix material respectively.

w_p, w_m, w_c - The weight of the reinforcement material, the matrix material, and the composite material respectively.

By using the hand lay-up method we prepare the polymer composites and hybrid polymer composites. Careful mixing of epoxy with nanoparticles in a beaker by using an ultrasonic processor at (30 minutes) to minimize voids and clustering of particles. The mixture was left to cool down at room temperature,

after that added the hardener to the mixture and mixed mechanically for (10 minutes) to obtain homogeneity. Finally, they have cast the mixture in molds, the samples were cutting depend on the tests.

In general, the samples used in the tests and examinations were prepared according to the standard system specifications, as follows:

- a. DSC test: (1cm X 1cm).
- b. Dielectric constant test: Diameter (20 mm).

and for thermal and dielectric tests:

- For DSC test: Using a (STA. PT-1000 Linseis) of (Linseis Company – Germany).
- For dielectric constant test: Using a (Agilent Impedance Analyzer 4294A) of (Taiwan).

3. Results and Discussion

3.1 DSC Test

a. Glass-Transition Temperature (T_g)

The glass transition is an endothermic phenomenon that happens within a temperatures range, after the glass transition arises, the material behavior stabilizes at temperatures range roughly to (320 °C) and the material is then subjected to thermal decomposition process, based on the form of the bundle and the energy needed to crack it [5]. The glass transition temperature (T_g) for epoxy was recorded before and after the reinforcement with nanoparticles (ZrO₂, CuO) with different weight ratios ((0, 0.3, 0.6, 0.9) wt%), by using the differential scanning calorimetric (DSC), figures from (1) to (3) show the values of the glass transition temperature for all the composites and as shown in table (1), where we notice that the glass transition temperature for pure epoxy is equal to (79 °C) and when reinforcement the epoxy with all nanoparticles we notice a change in the glass transition temperature, where we notice at composites (EP-ZrO₂, EP-CuO) that the the glass transition temperature increases with the increase in the weight ratio of the reinforcement reaching at the weight ratio (0.9 wt%) of the reinforcement, then the glass transition temperature at this weight ratio decreases with remaining the values of the glass transition temperature greater at the composite (EP-ZrO₂) and smaller at the composite (EP-CuO) respectively than the glass transition temperature of pure epoxy, as we can see at the hybrid composite (EP-CuO/ZrO₂) the glass transition temperature behaves erratically but stay all the values of the glass transition temperature (at all the weight ratios of reinforcement) of this hybrid composite are greater than the glass transition temperature for pure epoxy, the increase in the glass transition temperature by increasing the weight ratio of the reinforcement indicates the transformation of the material from the most flexible state to the least flexible state and that

this increase is evidence of the interconnection between the reinforcement material and the base material, by increasing the bonding of the reinforcement material with the base material, the rate of molecular weight increases and thus causes obstruction the movement of the polymeric chains, which need a higher amount of heat (energy) to reach the appropriate degree of freedom of movement to transfer to the rubber state and thus increase the glass transition temperature [6]. The decrease in the glass transition temperature may be due to the agglomeration of the reinforcement materials in the base material due to the large surface area (reinforcement materials) or the moisture absorption may be a cause of the decrease in the glass transition temperature [7].

Table 1. Glass transition temperature values of pure epoxy and reinforced with nanoparticles (ZrO₂, CuO) with different weight ratios

Weight ratio (wt %) of nanoparticles	Glass Transition Temperature (T _g) °C		
	EP-ZrO ₂	EP-CuO	EP-CuO/ZrO ₂
EP	79	79	79
0.3 %	82.22	82.12	86.28
0.6 %	89.97	85.12	79.18
0.9 %	83.05	78.82	83.64

b. Crystalline Melting Temperature (T_m)

The crystalline melting temperature is used to determine the nature and degree of purity of a substance [7]. The crystalline melting temperature (T_m) of epoxy was recorded before and after the reinforcement with nanoparticles (ZrO₂, CuO) with different weight ratios ((0, 0.3, 0.6, 0.9) wt%), by using the differential scanning calorimetric (DSC), figures from (1) to (3) show the values of the crystalline melting temperature for all the composites and as shown in table (2), where we notice that the crystalline melting temperature of pure epoxy is equal to (334.17 °C) and when reinforcement the epoxy with all nanoparticles a change in the crystalline melting temperature is observed, also we notice at the composites (EP-ZrO₂, EP-CuO, EP-CuO/ZrO₂) that the crystalline melting temperature increases with the increase in the weight ratio of the reinforcement reaching at the weight ratio (0.9 wt%) of the reinforcement, then the crystalline melting temperature at this weight ratio decreases with remaining the crystalline melting temperature values are greater than the crystal melting temperature of pure epoxy. The decrease in the crystalline melting temperature compared with pure epoxy is due to the irregularity, distribution, and homogeneity of the nanoparticles in the base material [8], and there is another reason for this decrease, which is the occurrence of an interaction

between the polymeric chains of the base material and the nanoparticles, which prevent the movement of these polymeric chains and thus reduce the crystalline melting temperature [9]. The increase and instability in the crystalline melting temperature are due to the high thermal stability of the nanoparticles and the interaction between the base material and the reinforcement materials [10]. This increase and decrease in the crystalline melting temperature compared with pure epoxy may be due to the accumulation of nanoparticle blocks in the base material, which leads to the creation of a protective barrier [10].

Table 2. Crystalline melting temperature values of pure epoxy and reinforced with nanoparticles (ZrO₂, CuO) with different weight ratios

Weight ratio (wt %) of nanoparticles	Crystalline Melting Temperature (T _m) °C		
	EP-ZrO ₂	EP-CuO	EP-CuO/ZrO ₂
EP	334.17	334.17	334.17
0.3 %	345.06	346.86	346.74
0.6 %	345.85	349.86	349.86
0.9 %	334.47	340.26	340.26

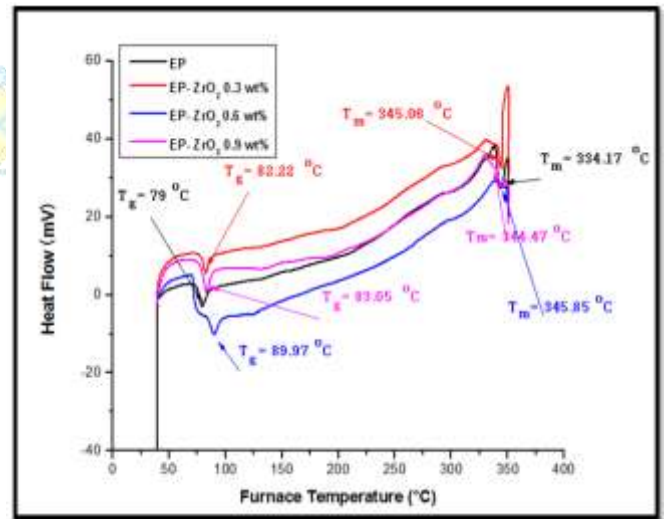


Figure 1. DSC thermal diagram of composite (EP-ZrO₂) with different weight ratios

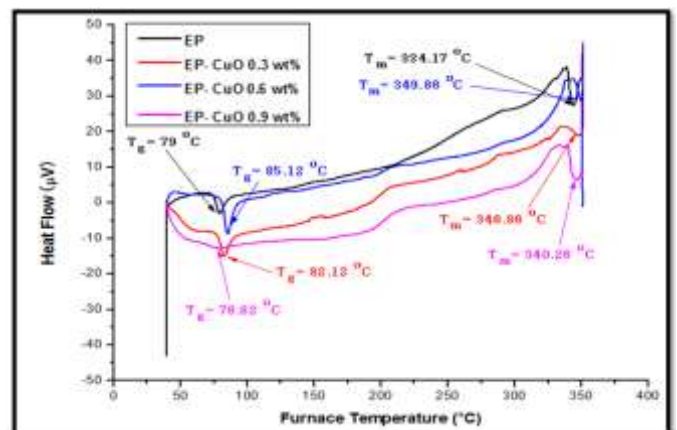


Figure 2. DSC thermal diagram of composite (EP-CuO) with different weight ratios

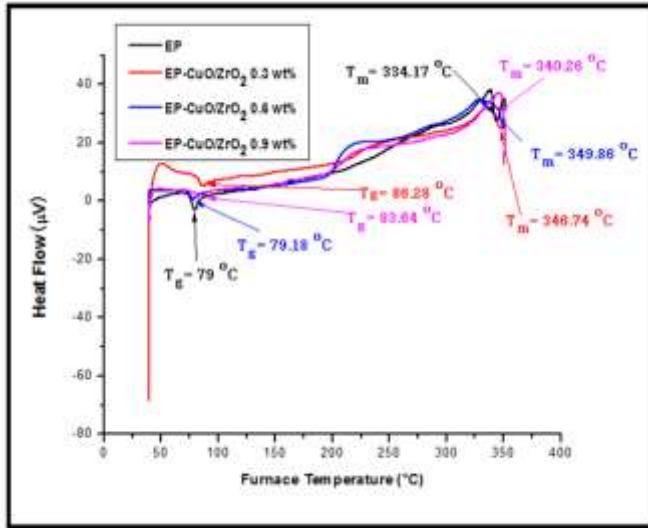


Figure 3. DSC thermal diagram of the hybrid composite (EP-CuO/ZrO₂) with different weight ratios

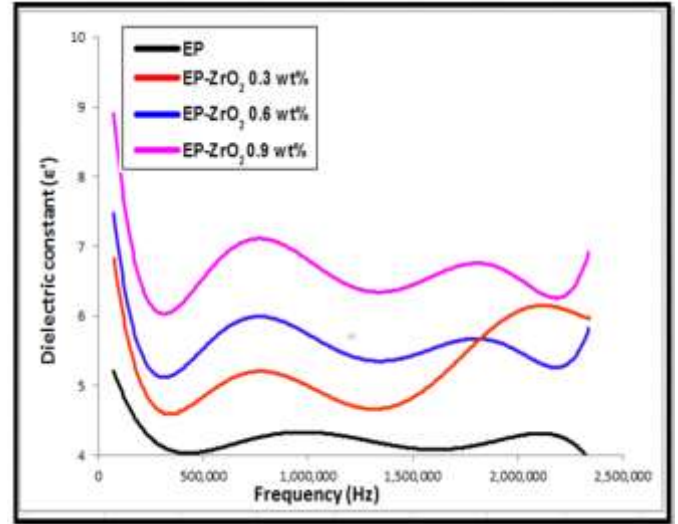


Figure 4. Dielectric constant as a function of frequency for composite (EP-ZrO₂) with different weight ratios

3.2 Dielectric Test

Dielectric constant: The dielectric constant of epoxy was recorded before and after the reinforcement with nanoparticles (ZrO₂, CuO) with different weight ratios ((0, 0.3, 0.6, 0.9) wt%) and with a range of frequencies (50Hz-5MHz) at room temperature and as shown in the figures from (4) to (6), where we notice that the dielectric constant decreases with increasing the frequency for all composites, and this behavior is known for electrically insulating materials [11], the effect of polarization is the reason for this, because the dielectric constant depends mainly on the mechanism of polarization of its different types (electronic polarization, ion polarization, directional polarization and the polarization which reduce from the interface surface) [12].

In the low frequencies region, all types of polarization occur, so we see the dielectric constant values as the largest possible, however, these high values of the dielectric constant are a result of the interface polarization due to its large value relative to other types of polarization, in the low frequencies region, the effect of polarization is more important because the molecules of the dielectric materials have sufficient relaxation time to direct them in the direction of the applied electric field when the voltage is applied, and after that, the polarization effect becomes insignificant at the high frequencies region because the particles do not have sufficient relaxation time to direct themselves in the direction of the applied alternating electric field.

The dielectric constant is not dependent on the frequency only, but also on the weight ratio of the reinforcement, Since we notice that the dielectric constant increases with the increase in the weight ratio of the reinforcement at the same frequency for all the composites due to the increase in polarity [13].

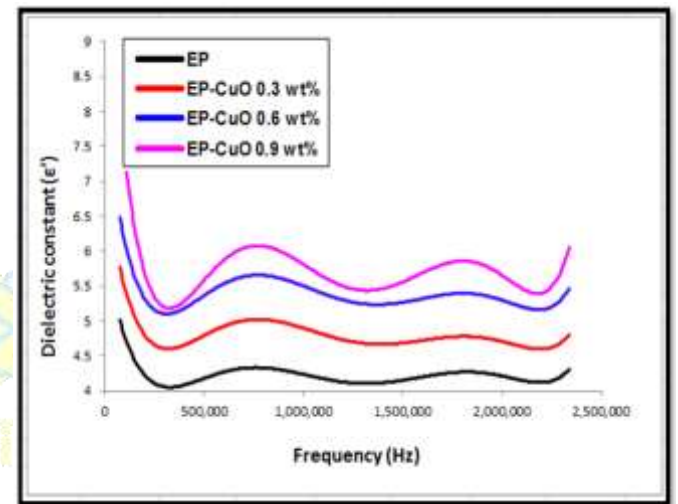


Figure 5. Dielectric constant as a function of frequency for composite (EP-CuO) with different weight ratios

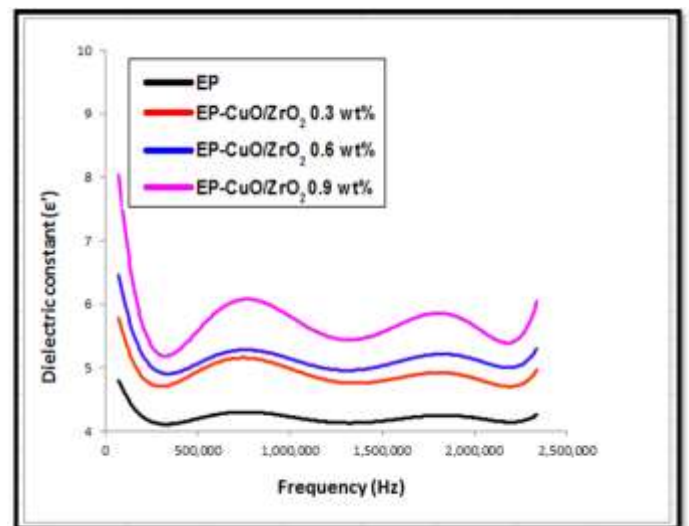


Figure 6. Dielectric constant as a function of frequency for the hybrid composite (EP-CuO/ZrO₂) with different weight ratios

4. Conclusions

A DSC test for pure epoxy showed that the glass transition temperature increased unevenly with the increase in the weight ratio of the reinforcement with nanoparticles, thus, these polymeric composites can be used as flame retardants. While the crystalline melting temperature increases unevenly with the increase in the weight ratio of the reinforcement in nanoparticles, but we note that the crystalline melting temperature exhibited an irregular behavior at some weight ratios of the reinforcement with nanoparticles compared with pure epoxy.

Increasing the dielectric constant with increasing the weight ratio of the reinforcement with nanoparticles at the same frequency for some polymeric composites, and the dielectric constant decreases with increasing the frequency for all polymeric composites and all weight ratios of the reinforcement, in the high frequencies region, these dielectric properties do not depend on the frequency and stay constant, indicating the possibility of applying these polymeric composites in devices that require stability in the dielectric properties at high frequencies.

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