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Dielectric Relaxation, Electric Conductivity and Thermodynamic Studies on Epoxy Polyurethane Blend and Their Composites

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Abstract: The purpose of this study is to improve the dielectric properties of epoxy-based polymer composites by adding rock and glass wool to achieve a relatively high dielectric constant and lower dispersion; hence the dielectric relaxation of composite materials which combines of epoxy/polyurethane reinforced with fibrous materials (rock wool (RW) and glass wool (GW)) with constant weight fraction of (10%) were investigated. The data of AC conductivity have been analyzed in the light of different theoretical models based on correlated barrier hopping (CBH) and Maxwell-Wagner model. The dielectric measurements were carried out for all samples over the frequency range of (10^2-10^7) Hz and over temperature range of (293-463) K^0. It is found that all samples displayed dielectric dispersion, thus the result for dielectric constant and dissipation factor give a direct evidence of the existence of Debye relaxation leaving a wide distribution of relaxation time. Eyring's relaxation rate equation have been used to determine the thermodynamic parameters, Gibbs free energy of activations and enthalpy for all samples. The results showed the existence of a stronger intermolecular interaction in all samples.

Keywords: Dielectric Constant, Dielectric Relaxation, Dissipation Factor, Epoxy-Based Polymer Composites, Relaxation Time

1. Introduction

Epoxy-based composites materials have several interesting over the past years due to their good properties such as superior strength, high hardness and durability, corrosion resistance, better thermal stability and good dielectric behavior, in addition to being lightweight materials with high good chemical corrosion resistance. and easy casting with low cost compared to other materials. [1-4]. However, epoxy/ polyurethane reinforced by fiber material such as glass wool and rock wool, possess outstanding characteristics such as high dielectric constant and good thermal stability, low density and hence high specific stiffness and strength which make them highly suitable for used in the manufacturing technology [5-11]. However; such characteristics in an epoxy require high levels of cross linking which usually results in brittle behavior. It is well known that some brittle epoxy polymers can be toughened by addition of a rubbery phase. For example, epoxy resins have been used as an encapsulation of semiconductor devices and chips, as the capacitance of semiconductor chips or devices increases the heat dissipation caused increases the cracks produce on epoxy surface [11]. These cracks play a major role of leakage currents in semiconductor chips. Most epoxy- based composite materials developed to improve their mechanical, thermal and dielectric properties, this development depends on the type and the geometry of the reinforcement materials.

Studying dielectric insulation at multiple temperatures and frequencies is particularly interesting because of the nature of polymeric composites that have long chains and high molecular weight. It is known that most of the dielectric properties such as (dielectric constant, dissipation factor, relaxation time, and elastic dispersion) in polymer composites materials are dispersed even at low frequencies, and this behavior reflects relatively high activation energies for the molecules unit movement and the chain segment, or is dispersed at high frequencies, which reflects low activation energies. Relative to the unit movement of the molecules and

ions [11, 12]. The dispersion can be either non-cooperative or cooperative depending on the degree of correlation with other relaxations. The study of dielectric relaxation provides available tool for gaining some knowledge of the kinetic of molecule interaction in polar materials [13]. In light of this, in this paper, epoxy and polyurethane resins are blended to use as the matrix for the composite. Then, rock and glass wool were added at a fixed weight ratio of (10%) in order to improve the dielectric properties by increasing the value of the dielectric constant and the dissipation factor (tan δ) and prolonging the relaxation time (τ) for the PU/EP- composites. These treatments would also improve the thermodynamic constants of the polymer composite, which increases the chances of its use in the industrial and engineering applications.

2. Experimental.

2.1. Materials and Method

The epoxy resins (DGEBA, YD-128) are low molecular weight liquids with epoxide equivalent weight of 176g. The curing agent phthalic anhydride (PA) used in this study was supplied by Kukdo Chem. Co. of Korea. The polyurethane (PU) resins was a commercial resin type (TEK-CAST) supplied by TEKCAST- Industries New Rochelle NY.10801(USA) along with a curator Isocyanides (HYG). The glass wool used in this study consist of 56 %(SiO_2), 15.5 % (CaO), 15 % (Al_2O_3) and 3.5 % (Mg O), and rock (Basalt) wool are supplied by (TEKCAST Industries –New Rochelle. NY. USA).

2.2. Morphology of Wool Fibers

Figure 1 shows the digital photos of the chopped rock wool and glass wool fibers used in this article. As shown in Figure 1(a), the chopped rock wool fibers are calcified, the length of the fiber is about 0.2–1 mm. In Figure 1(b), the glass wool fibers are agglomerate, the length of the fiber is about 0.5-2mm; the fiber surface is generally smooth; some particles can be seen on the fiber surface.

a b

Figure 1. *a: the digital photo of rock wool; b: the digital photo of glass wool.*

2.3. Samples Preparation

An open-mold casting technique was used to perform the epoxy/polyurethane blends and their composites in this study. Epoxy and polyurethane blends were prepared in this study with different weight fractions (90%-10%), (80%-20%), and (70%-30%), where the blend (80%-20%) was chosen to prepare the composite sheets by adding a fixed weight fraction (10%) of rock wool and glass wool with constant thickness of 0.5mm.

2.4. Measurements

The dielectric measurement was performed using three electrodes method (Guarding electrode method). The specimen was fixed in specimen holder and placed into temperature controlled oven type (Heresies electronic). High and low holder terminals are connected to dielectric analyzer type Hewlett Packard model (HP4274A & HP4275A), the third holder terminal was connected to the earth. Three dielectric parameters were measured directly from above setup total resistance (R_T), total capacitance (C_T) and dissipation factor tanδ with an accuracy of (0.1%).

3. Results and Discussion

3.1. AC Conductivity

In this part of study, we report the effect of, temperature, frequency and type of reinforcement material on AC conductivity. Figure 2 shows the variation of AC conductivity as a function of frequency at various temperatures (293-443) K^0, for EP80%/PU20% blend and EP/PU-RW, EP/PU-GW composites. The results showed a weak dependence of alternating conductivity on frequency in the range (10^2-10^4) Hz in all samples tested. This behavior can be attributed to the interstitial polarization which is slightly change, so that this polarization is dominant over this range. The rock wool and glass wool composites are show similar behavior through the frequencies range over (10^3- 10^7) Hz at all indicated temperature. These two composites are show a rapidly increases on conductivity at frequencies greater than 10^4 Hz to reach the values of 1.06×10^{-6} (S/cm) and1.13×10^{-6} (S/cm) at 1MHz for rock and glass wool

composites respectively. These results indicate that the additives improved the conductivity of the polymers. Under these circumstances, one may further analyze the characteristic of composites on the basis of the Maxwell-Wagner model [14]. Through this, two extreme types of system can be identified that consist of two chopped phases dispersed in a continuous matrix.

The transport properties of the main matrix series segmental particles of both dispersed phases (PU and wool) are affected by processes whose origin at or near the boundaries between the phases.

The transport properties of segmental PU particles are improved by wool dispersed at or near the boundary between two phases.

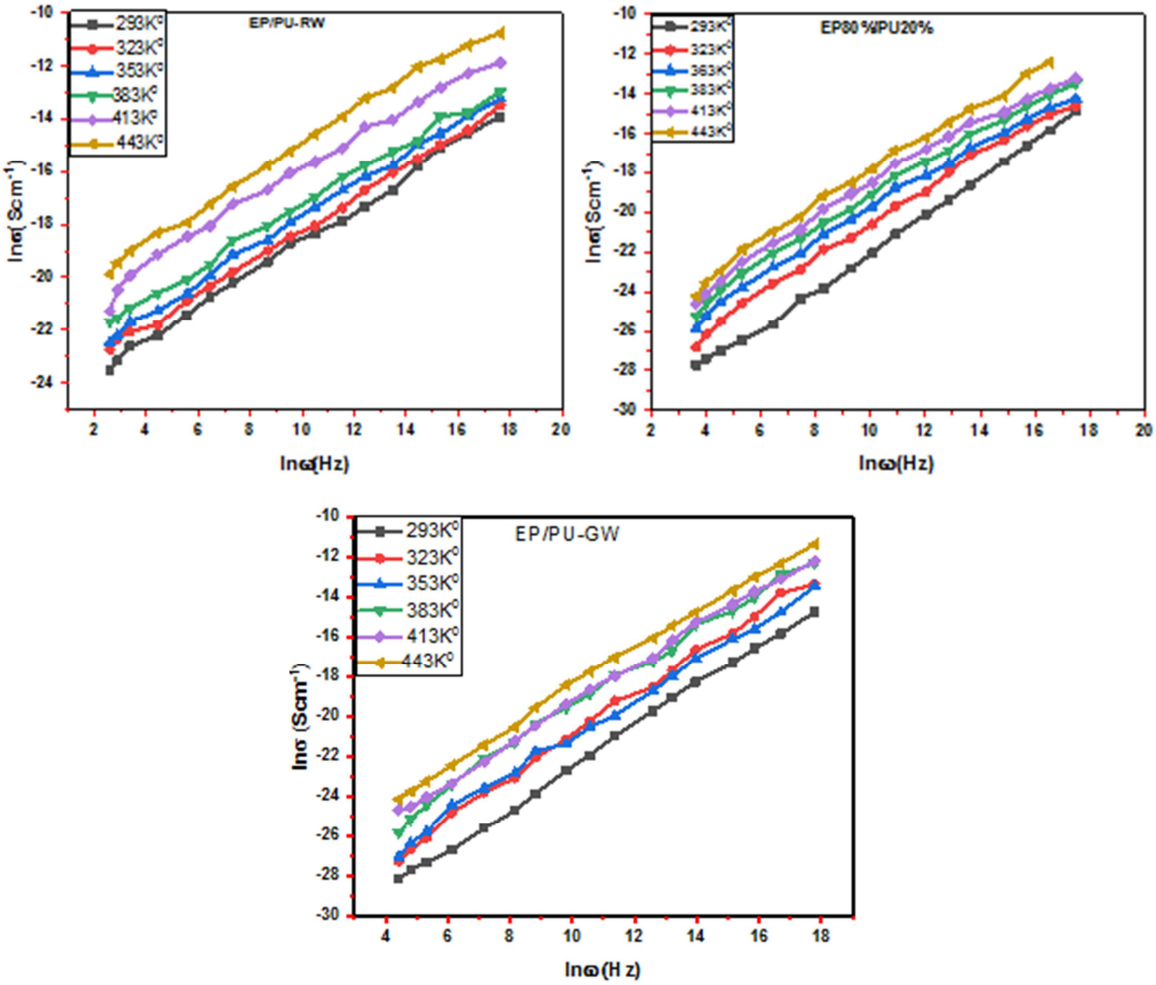


Figure 2. *Electrical conductivity of EP/PU blend and EP/PU-RW, EP/PU-GW Composites at different frequencies.*

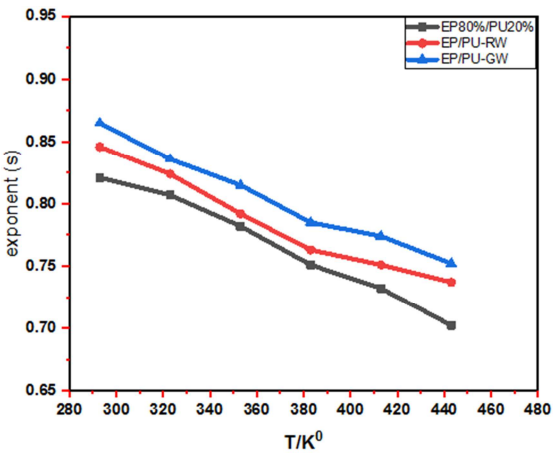


Figure 3. *The Exponent (s) of EP/PU blend and EP/PU-RW, EP/PU-GW Composites at different temperatures.*

Figure 3 shows the variation of exponent (s) as a function of the temperature, the values of exponent (s) were extracted from the slope of the curves of AC conductivity versus frequencies. The results reveals that the exponent (s) values are less than unity for all samples, also these values are decreased with temperature increasing. This result is typical to the ordinary behavior of the dielectric materials which can be explains by correlated barrier hopping model (CBH) [15].

3.2. Dielectric Relaxation Study

The values of the real and imaginary parts of the dielectric constant were determined by measuring the electrical capacitance (C), dispersion factor (tan δ), and the total resistance (R) for all samples. Figure 4 show the variation of the real part (ε_r) as a function of frequency at various temperatures for EP/PU blend and their composites. The

result showed that the values of (ε_r) were affected by the addition of the reinforcing material. As well as the high dependence of the real part of the dielectric constant on the frequency in the range exceeding (10^2-10^5) Hz for rock wool and glass wool compounds, this result can be explained by Pohl and Pollack model [16]; they are proposing that an intra-chain transport mechanism involving polarons. This mechanism does allow an explanation of usually high dielectric constants and associated phenomenon of nomadic polarization observed in many polymer composites. The result also showed a weak effect of (ε_r) by temperature for all samples tested over the range (293-343) K. Thus at this range the thermal activation of the conductivity is almost neglected, since the motion of main chain had been a dominate mechanism of conduction, but at temperature greater than 343 K, the values of (ε_r) increase rapidly with increasing temperature. Hence the ions motion becomes easiest due to transform the composite from glassy to rubbery state [17]. We can say that the behavior of the EP/PU blend and its composites is consistent with Debye dispersion of the dielectric layers. [18].

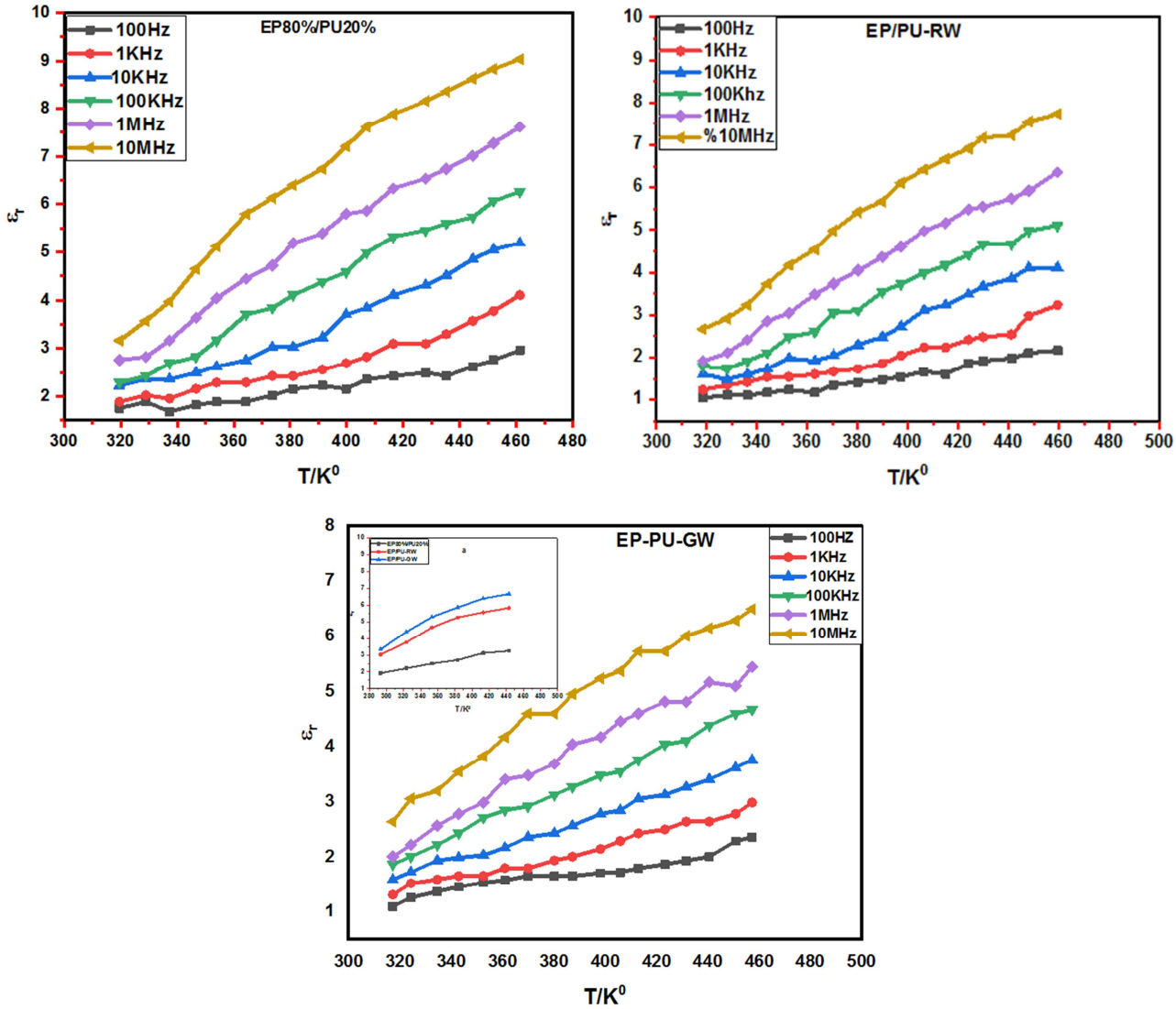


Figure 4. *The real part of EP/PU blend and EP/PU-RW, EP/PU-GW Composites at different temperatures and frequencies, Inset Figure shows the comparison between the blend and their composites.*

Figure 5 show the variation of the imaginary part of dielectric constant (ε_i) as a function of temperature at various frequencies for EP/PU blend and their composites. It is clear from Figure 5 that there is a gradual increase in the value of the (ε_i) at low temperatures, which rises sharply at higher temperatures due to thermal activation resulting by thermal defects [17].

Figure 6 show the variation of dissipation factor (tan (δ)) as a function of temperature at various frequencies for studied composites. The result shows that the EP/PU-RW and EP/PU-GW composites reveal similar behavior. Hence the tan (δ) is showing slight increased with increasing temperature over the range 293-343 K. In this range the electrode polarization is dominated mechanism [19]. At temperature greater than 353K a pronounced loss peaks have been existing; these peaks related to α-relaxation which is

associated with micro-Brownian motion of amorphous main chain [20, 21].

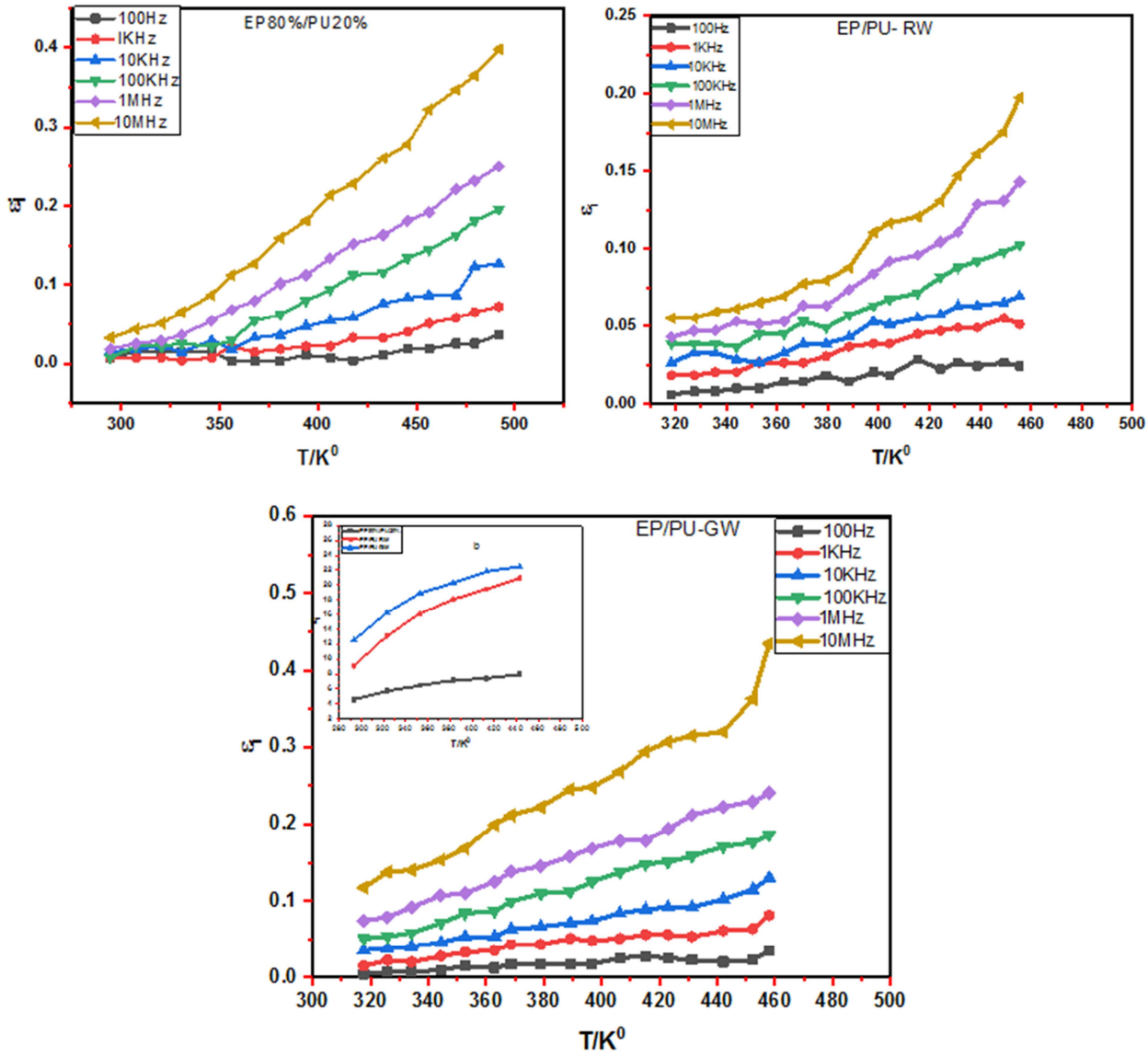
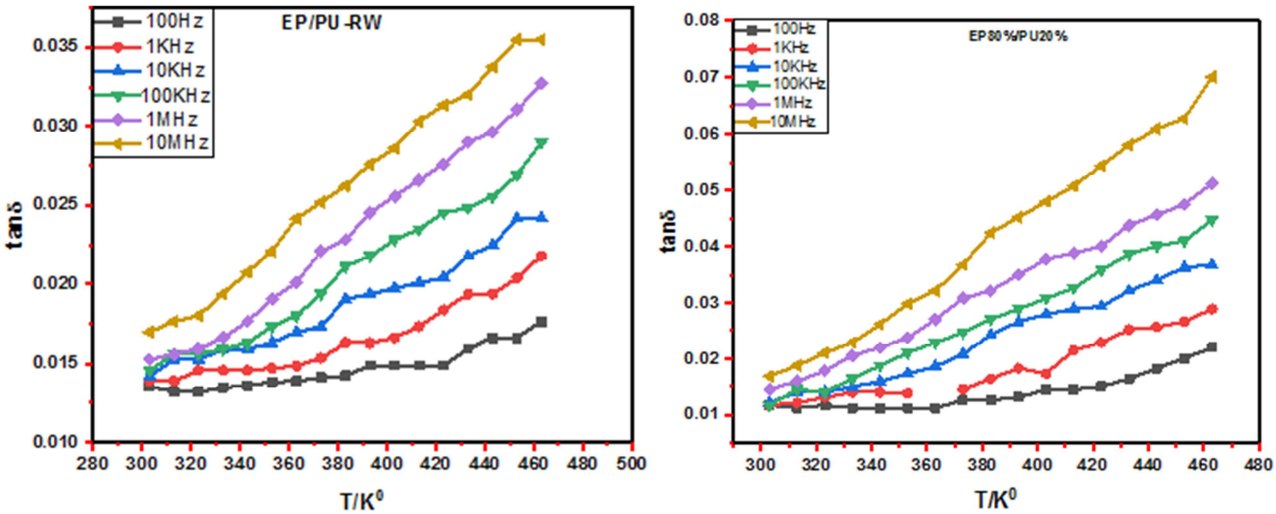


Figure 5. *The imaginary part of EP/PU blend and EP/PU-RW, EP/PU-GW Composites at different temperatures and frequencies, Inset Figure shows the comparison between the blend and their composites.*



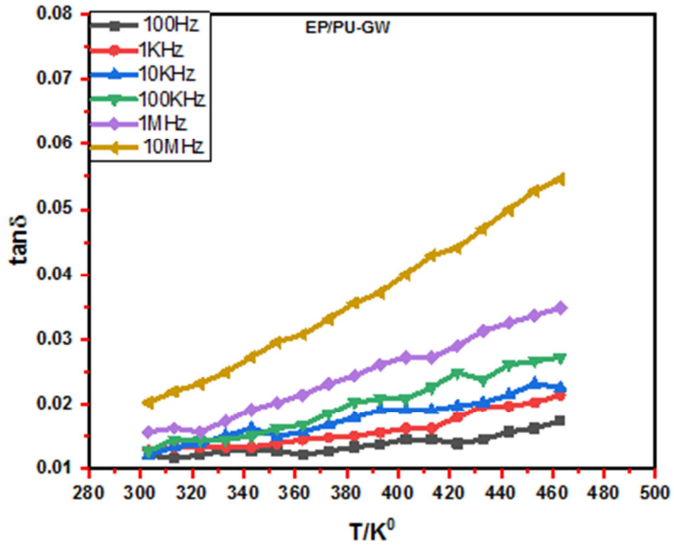


Figure 6. *The dissipation factor (tan δ) of EP/PU blend and EP/PU-RW, EP/PU-GW Composites at different temperatures and frequencies.*

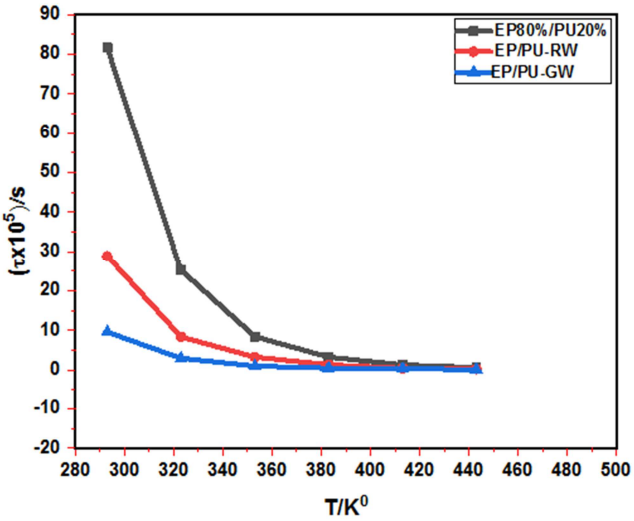


Figure 7. *The relaxation time (τ) of EP/PU blend and EP/PU-RW, EP/PU-GW Composites at different temperatures.*

Figure 7 show Purifies change of molecular relaxation time (τ) decreased with increasing the temperature for EP/PU blend and their composites. This result is in agreement with the concept of molecular relaxation; the reason of this behavior is the influence of the segmental molecular interaction energy decreased with increasing the temperature [22-23].

3.3. Thermodynamic Parameters

The thermodynamic parameters (Gibbs free energy (ΔG), and entropy (ΔS)) of EP/PU blends and their composites, were determined by Eyring's relaxation rate equation, and the slopes of relaxation time (τ) versus temperature. Figure 8(a, b) show that the Gibbs free energy (ΔG) and entropy (ΔS) showed increases with increasing temperature for all tested samples, this temperature dependence related to the amount of thermal energy that Absorbed by polymer chains. Which leads to higher deterministic motion of molecules [23].

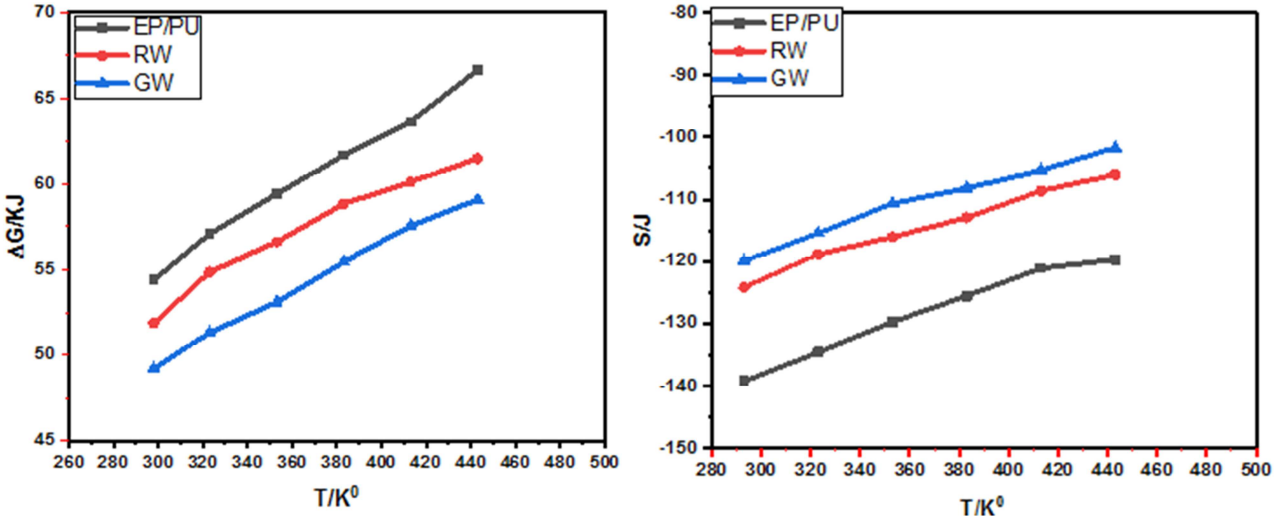


Figure 8. *Gibbs free energy (ΔG), and entropy (ΔS) of EP/PU blend and EP/PU-RW, EP/PU-GW Composites at different temperatures.*

4. Conclusions

The imbedding additive materials rock wool (RW), glass wool (GW) into the EP/ PU polymer blend improve the AC conductivity ($\sigma_{a.c}$) and affected the real part (ε_r) imaginary part (ε_i) of the dielectric constant As well as the loss coefficient (tanδ). Also we note the adding of dispersive phase reduce the values of the exponent (s) and the relaxation time (τ). The thermodynamic parameters Gibbs free energy (ΔG), and entropy (ΔS) are estimated by dielectric measurements according to Eyring theory. It is found that the composites possess high values of (ΔG).

Conflicts of Interest

The authors declare no conflicts of interest.

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