ZnO Polymer Nano Composites Synthesis, Characterization, and Thermo-Mechanical Property Comparison

J. C. Chrislin Mario[1], Y. Christabel Shaji[1]*, Y. Brucely S[2]. Ajith Sinthuja[3], A. Bovas Herbert Bejaxhin[4] and N.Ramanan[5]

[1,3]*Department of Chemistry, Holy Cross College (Autonomous), Nagercoil-629004, Tamil Nadu, India. *E-mail: christabelshaji@holycrossngl.edu.in*
[2]*Research Department of Physics, Holy Cross College (Autonomous), Nagercoil 629004, Tamil Nadu, India.*
[2]*Department of Mechanical Engineering, SRM TRP Engineering College, Irungalur, Tirchirappali, Tamil Nadu, India.*
[4]*Associate Professor, Department of Mechanical Engineering, Saveetha School of Engineering, SIMATS, Chennai. E-mail: herbert.mech2007@gmail.com*
[5]*Assistant Professor, PSN Engineering College, Tirunelveli. Ramananinjs2020@gmail.com.*

Abstract

Both the polyester resin matrix-based polymer ZnO nano composites and pure polyester sheet were synthesised using the solution casting method. The crystalline structure of the nano-particles was examined inside using X-ray diffraction (XRD). The fundamental polymer composition, additives, organic contaminants, and purity were all assessed by FTIR. A minor alteration in the absorption bands was seen in the polyester system with ZnO added. The thermal properties were examined using differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA), and the results unmistakably demonstrated the creation of a highly cross-linked polyester molecular structure or improved free volume fractions in polymer nano composites. A mechanical analyzer's tensile and flexural strength tests revealed the potential for nanoparticle aggregation due to a strong interaction with resin. To calculate the relative permittivity and the loss of tangents (tan), dielectric studies had been used. Analysis of the hydrophobic properties of the pure and ZnO polyester nano composite.

Keywords: Polyester resin, Polymer ZnO Nano composites, Pure polyester sheet, Thermal, Mechanical properties, Dielectric spectroscopy, Hydrophobic character.

1.0 Introduction

Thermosetting resins and the composites made from them are widely used in a number of applications due to their remarkable properties and low cost [1-3]. In order to preserve the resins from environmental deterioration, inorganic particles are also added; nevertheless, the addition of several common inorganic particles has a tendency to decrease the material's strength and transparency. The strength of the material is not in any way diminished by this binding process because nano-particles typically have a more active surface and bind to the resins with sufficient strength. As a result, a sizable amount of research has focused on using nano-particles to improve thermosetting resins [4]. ZnO nano-particles, also referred to as ZnO NPs, have a strong absorption ability. It can be used on matrices to protect them from environmental effects and increase the tensile strength of the materials [5]. The material's smaller diameter and the

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*Corresponding Author

relatively tiny amount of additives it contains have no effect on its transparency, either [6]. Despite the high cost and limited availability of materials for surface films, the price of nano-particles is falling as technology progresses. Therefore, the glass fibre reinforced polymer sector will gain from the usage of ZnO NPs to stabilise unsaturated polyesters. This research conducts a thorough investigation of the thermal stability, tensile strength, flexural strength, and hydrophobicity of the pure polyester and ZnO added polyester Nano composites.

2.0 Experimental Specifics

Creation of ZnO NPs

Zinc nitrate and sodium hydroxide were employed as the precursors in co-precipitation to create ZnO nano-particles. In this experiment, the proportion of zinc nitrate to sodium hydroxide was 1:2. First, 100 millilitres of water were used to dissolve 26 grammes of zinc nitrate. Next, 8 grammes of sodium hydroxide were added, and both solutions were then left aside. This effort involved maintaining an aqueous solution of zinc nitrate under continuous stirring using a magnetic stirrer to make sure the zinc nitrate was completely dissolved. In a similar way, a sodium hydroxide aqueous solution was created by stirring the components for an entire hour. A solution of sodium hydroxide was then gradually added, while the mixture was repeatedly agitated at high speed, after the zinc nitrate had completely dissolved. The reaction was allowed to run for about 15 minutes after adding all of the sodium hydroxide so that it could advance. After being sealed, the beaker was left in this condition. The supernatant liquid was painstakingly removed from the combination after the solution was allowed to settle for a whole night. For around two to three days, this therapy was given every day. The solution was ultimately filtered, and either the substance or the precipitate was extracted and eliminated separately. It was then dried and kept at a temperature of 600 degrees Celsius for two hours in a muffle furnace. During the calcination process, zinc hydroxide completely transforms into zinc oxide nano-particles.

Synthesis of pure polyester sheet

Two separate beakers were used to hold the hardener, which weighed 0.5 grammes, and the polyester resin, which weighed 30 grammes. The polyester resin was continuously stirred using a mechanical stirrer for roughly fifteen minutes. The hardener was then added, and the resin mixture was manually mixed with a stir stick. One drop of the catalyst was then added and combined with this. Following that, the slurry was poured into the metal mould. It was left at room temperature undisturbed for roughly 4-5 hours. The artificial sheet could then be removed from the mould. As a result, a tidy and delicate polyester sheet was produced.

Nano composites made of ZnO and polyester were made

The ZnO NPs were initially dispersed into 30 grammes of resin at a weight percentage of 1 after the two components had been combined for a whole day using a high-speed mechanical stirrer. The liquid was then mixed before 0.5 grammes of the hardener were added. Last but not least, 1 drop of catalyst was added and well blended by hand stirring. Following that, the slurry was poured into the metal mould. It was left at room temperature undisturbed for roughly 4-5 hours. The synthetic sheet could then be taken out of the mould. As a result, a fine and tidy polyester sheet with ZnO addition was produced. To obtain more nano composite sheets, this process was repeated.

Figure 1: Image of pure Nano Composites with ZnO applied

Identification Methods

The XPERT-PRO diffractometer system (PW 3050) with automated data collection and CuK radiation (= 1.5406) operating at 40 kV/30 mA is utilised as the main piece of apparatus when performing X-ray diffraction. Using a SHIMADZU type IR Affinity-1 instrument, measurements for Fourier Transform Infrared Spectroscopy (FTIR) were made on the materials in the wavelength range of 4000-400 cm1. For the FTIR examination of the material, transmission was the mode used. Differential scanning both the examination into the thermal characteristics included calorimetry and thermo gravimetric analysis. From 20 degrees Celsius to 800 degrees Celsius, 3 to 5 mg of dry material were heated at a scan speed of 10^oC per minute. The standards were kept in ceramic

sample containers, while the composites were kept in aluminium pans. Aluminum was used to make both kinds of containers. For TG, a range of 35000mg was employed, whereas a range of 5000V was used for DSC. Using a mechanical analyzer set to the tensile test mode, the produced sheets were put through a tensile test. The ASTM D 638 test standard was followed during this procedure. Utilizing a three-point bending approach, the flexural test was performed using a Japanese Shimadzu ASTM D790 standard testing apparatus. The machine had a range of 1-100 KN. Utilizing the instrument HIOKI 3532-50 LCR Hitester, dielectric experiments were conducted across a frequency range of 101 - 106 Hz, at three temperatures of 50°C, 100°C, and 150°C to estimate the relative permittivity and loss tangents (tan).
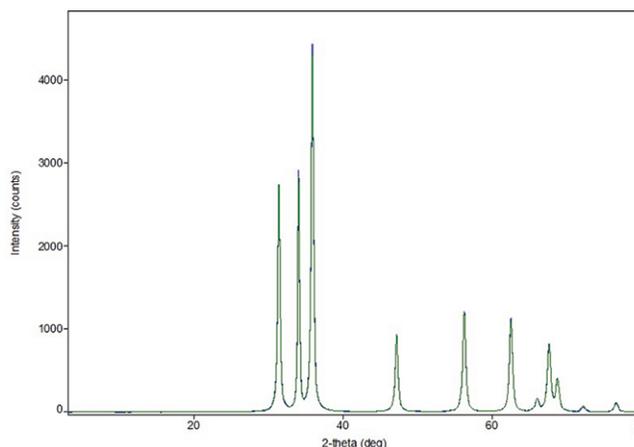

Figure 2: XRD pattern of 600°C-calcined ZnO NPs

3.0 Results and analysis

XRD evaluation

For produced ZnO nano-particles, powder XRD is utilised to determine the crystal phase as well as an estimate of the crystallite size. The 0.05° step size and 2.0 second capture period are used to acquire the diffraction patterns in the 2 range of (0°-80°). The XRD pattern of the produced ZnO nano-particles that were calcined at 600°C is shown in Figure 2.

The annealed ZnO NPs at 600 degrees Celsius took on a crystalline shape, as evidenced by the XRD pattern. Conclusion: The ZnO NPs made using the co-precipitation method show enhanced structure as the temperature is increased to 600 degrees Celsius. Furthermore, the generated ZnO nano-particles were measured and determined to be 49.02

nm in size, demonstrating the nanoscale nature of the ZnO NPs that were created. The X-ray diffraction spectra offer unmistakable proof that pure ZnO nanopowder has a crystalline structure in its natural state.

FTIR evaluation

The pure polyester and polyester-ZnO nano composite samples are made, and their characteristics are examined using Fourier Transform Infra-red (FTIR) spectroscopy. Below is a clear picture of the sample's FTIR spectrum and assignments for ready samples.

The frequency of the absorption band that appears at 3489 cm1 in the FTIR spectrum can be used to detect the presence of -OH stretching vibrations. The aromatic ring's

Table 1: ZnO NPs that were calculated using XRD at 600

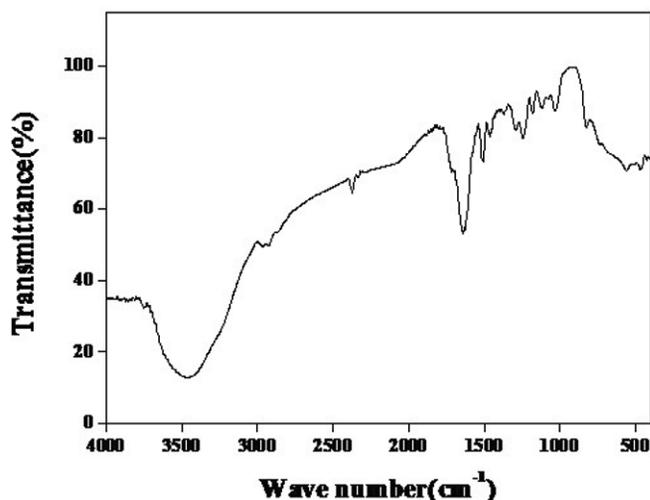|	Peak region (2θ)	D (ang)	FWHM (deg)	Size of a crystallite (nm)
1.	31.32	2.8535	0.335	55.237
2.	33.96	2.6374	0.258	53.051
3.	35.81	2.5053	0.351	52.785
4.	47.13	1.9268	0.371	50.849
5.	56.16	1.6363	0.399	48.940
6.	62.43	1.4861	0.410	47.437
7.	65.47	1.4250	0.500	46.608
8.	65.99	1.4145	0.430	46.583
9.	67.56	1.3853	0.449	47.437
10.	68.69	1.3653	0.448	46.660
11.	72.20	1.3073	0.470	46.583
12.	76.55	1.2435	0.400	46.106

Figure 3: FTIR range of 100% polyester
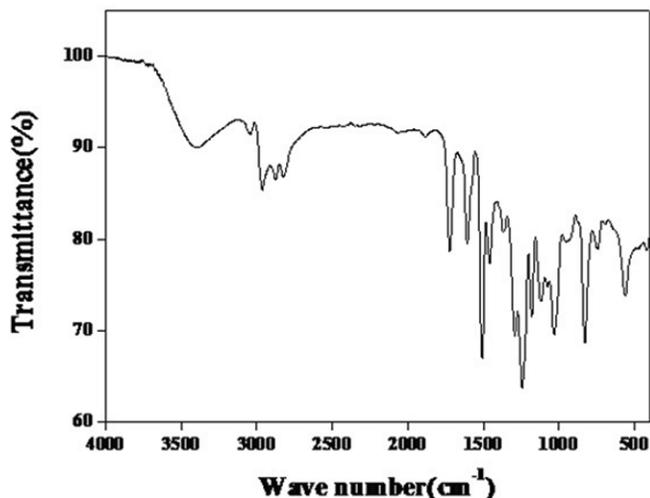
Figure 4: FTIR of polyester with 1% weight ZnO

C=C stretching is what generates the signal at 1611 cm-1. The absorption signal that occurred at a wavelength of 1745 cm-1 was caused by the ester group's C=O stretching. The peak for O-C stretching vibration, which was previously at 1239 cm1 in the spectrum of pure ester, has migrated to 1244 cm1 in the spectrum of ZnO filled polyester. The methyl group's C-H is being stretched when it stretches to form the absorption peak at 2922 cm1. Aryl ester carbonyl stretching vibration correlates to a prominent distinctive absorption peak between 1720 and 1740 cm1. The spectra reveals the stretched CH2 groups' absorption peaks at 2965 cm-1 and 2873 cm-1, respectively. Due to the strong adhesion of ZnO particles to polyester, a small shift in these absorption bands is seen when compared to those of pure polyester. Moreover, the ZnO added polyester shows good transmittance at the region 3700 cm–1

- 3800 cm–1. Therefore, this area represents the Zn-OH group that is not hydrogen bonded. A band at 824, 831, and 825 cm1 on the ZnO-filled polyester also corresponds to the bending vibration of cis-RCH=CHR. Since this is missing in pure polyester, there may be Zn-O-Zn group absorption because of a strong Zn-O-Zn band that exists in this range.

Thermal attributes

Differential scanning analysis to examine the thermal properties, calorimetry and thermo gravimetric analyses are performed. Pure polyester and ZnO/polyester systems have very similar breakdown profiles, and the degradation process takes place in two separate states. To establish the relative thermal stability of these materials, the temperature at which polyester nano composites degrade were tested over a range of weight loss percentages. The thermal stability of Nano Composites with ZnO nano-filler added has been reported to have a little increase when compared to the thermal stability of pure polyester. This could be the result of greater free volume fractions in polymer nano composites, or it could be the result of the spatial blockage brought on by nano-particles during the construction of a strongly cross-linked molecular structure of polyester. Table 2 provides an examination of the thermal behaviours of the samples that were created.

Table 2: Nano Composites with pure and ZnO-added TGA data

Model code	$T_{50}C$
Absolute polyester	420
Polyester+ 1wt % ZnO	480

Tensile power

Tensile strength is a measure of a material's ability to withstand forces that would otherwise cause it to break. The material's capacity to stretch before breaking is also indicated by the material's tensile strength. A computerised universal testing device from Shimadzu in Japan, with a range of 1-100 KN, was used to measure the tensile strength. In compliance with the ASTM D 638 standard, the test was conducted. Here are the measurements' descriptions: The test specimen utilised in the experiment had the following measurements: 150 mm in length, 25 mm in breadth, and t inches in thickness. The tensile strength of polyester nano composites with ZnO filler added has been proven to be much higher when compared to pure polyester nano composite. This suggests that intense contact with resin may have caused a nano-particle aggregation. Tensile strength values for pure and ZnO Nano filler (1wt%) added polyester nano composites are shown in Table 3.

Table 3: Tensile strength of pure and nanocomposite materials with ZnO

Sample	Elongation at break (%)	Maximum Load (N)
Pure polyester	1.7622	48.4 kg
Polyester+1 wt % ZnO	2.9997	81 kg

Flexural power

Flexural strength is the ability of a composite material to withstand bending forces that are applied in a direction perpendicular to its longitudinal axis. The ASTM D790 standard testing device, made in Japan by Shimadzu, is used to conduct the flexural test using a 3-point bending approach. The machine's range is 1-100 KN. The test specimen used in the experiment had dimensions of 1 cm in length, 2.5 cm in breadth, and 0.4 cm in thickness. When compared to a pure polyester sheet, the ZnO added polyester sheet has a higher flexural strength. The length of the chain affects the increase in flexural strength. Furthermore, the vanderwaals bond, a weak bond with high numbers, is the reason why the flexural strength is stronger for polyester resin with ZnO added. The

Table 4: Flexural strength of pure and nanocomposite materials with ZnO

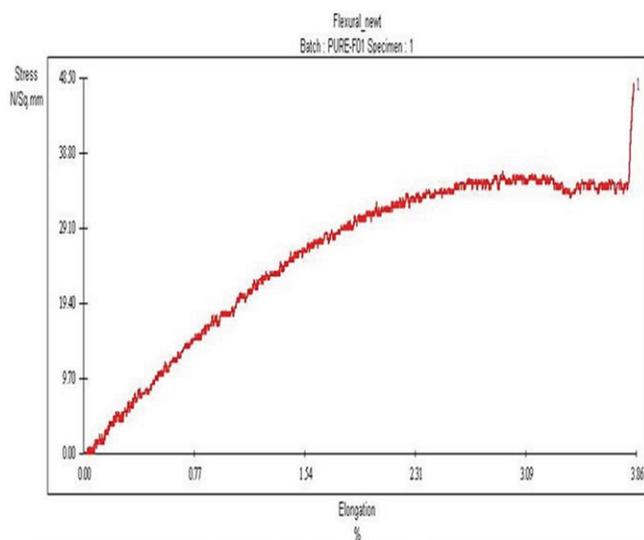| Sample	Ultimate Flexural Strength	Flexural Modulus (GPA)
Absolute polyester	95.13	2.45587N
Polyester + 1wt % ZnO	78.21	3.2190N

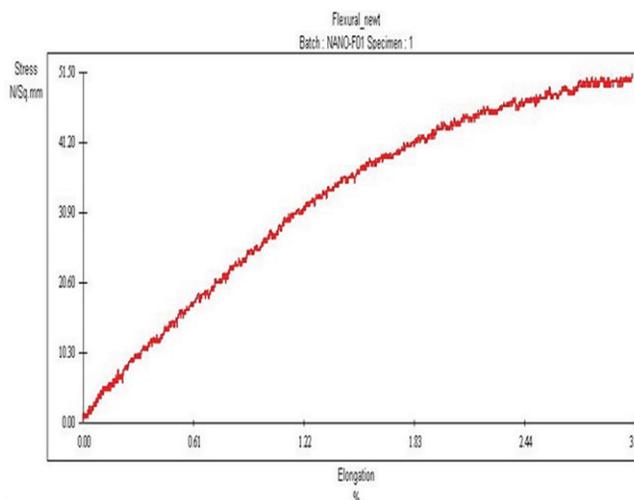**Figure 5:** Flexibility of polyester in its purest form

Figure 6: Flexural resistance of nanoscale ZnO composites

value of flexural strength for pure and ZnO (1wt%) added polyester nano composites is displayed in Table 4.

Dielectric research

The sample's AC conductivity is identified in the current investigation. Dielectric tests utilising the instrument HIOKI 3532-50 LCR Hitester, spanning a frequency range of 101-106 Hz, at three temperatures of 50°C, 100°C, and 150°C, are used to calculate the relative permittivity and the loss tangents (tan) [7]. The sample is prepared with dimensions of 7.5 × 64 mm for testing. Room temperature is maintained during all measurements, and the applied voltage is set at 1V. Below is a table listing the dielectric measurements and graphs.

Table 5: Permittivity of Pure Polyester Relatively

Frequency (Hz)	Temperature		
	50	100	150
50	1.4635	1.6506	1.4317
100	0.1349	0.39378	0.1618
500	0.2435	0.271	0.2575
1000	0.2262	0.2175	0.2386
5000	0.1679	0.1747	0.1786
10000	0.1421	0.1456	0.1576
50000	0.156	0.1606	0.1585
100000	0.151	0.1523	0.1535
500000	0.1418	0.1434	0.1449
1 M	0.1451	0.1463	0.1472
5 M	0.1557	0.1564	0.1569

Table 6: Polyester relative permittivity plus 1% weight ZnO

Frequency (Hz)	Temperature		
	50	100	150
50	0.7883	0.8574	1.6826
100	0.2033	0.2749	0.1779
500	0.1835	0.1697	0.2225
1000	0.1718	0.1647	0.2172
5000	0.1455	0.1344	0.1623
10000	0.1289	0.1257	0.1406
50000	0.1205	0.1207	0.1533
100000	0.1173	0.117	0.1492
500000	0.112	0.1125	0.1417
1 M	0.1145	0.114	0.1439
5 M	0.117	0.1153	0.1571

Figure 7: Frequency vs. Relative Permittivity at 100°C

Figure 7 shows that as temperature rises, the relative permittivity rises as well. It is clear that the effective permittivity of the polyester/ZnO nano-composite and unfilled polyester both rises with decreasing frequency. The fundamental reason for the relative permittivity's decline with frequency was the loss of polarisation brought on by dipolar groups in both polymers and nano-particles. The permittivity increases because all of the free dipolar functional groups in the polyester chain can orient themselves more easily at lower frequencies. Larger dipolar groups find it more difficult to align themselves with the alternating field as the electric field's frequency rises. As a result, these dipolar groups' contributions to the permittivity continue to decline, which ultimately causes the permittivity to degrade over time [8].
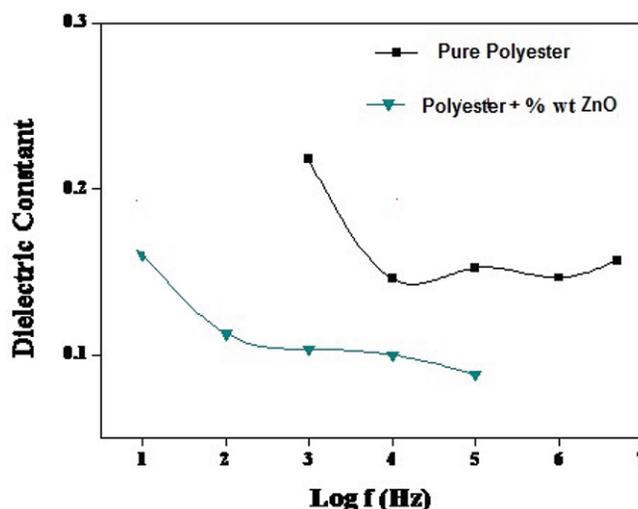
A hydrophobic personality

One of the most appealing and useful qualities that has not been extensively investigated in the past is the exceptional barrier capability with greatly decreased permeability to moisture and gases. The material also possesses thermal and mechanical properties in addition to this one. Due to zinc oxide nano-particles' inherent hydrophobicity, their incorporation into resin causes a decrease in the proportion of water absorption, represented as a percentage, in accordance with the percentage concentration. Another theory is that it results from the hydrogen bonds between the polyester and zinc oxide, which promote molecularly tight packing. In comparison with the pure polyester matrix, the ZnO doped polyester nano composites exhibit improved hydrophobic characteristics. Additionally, these nano composites have been noted for having outstanding mechanical qualities.

Table 7: Proportion of pure polyester sheet that swells

Number of days	Initial polyester sheet weight	Final polyester sheet weight	Weigh differently	Percent swelling
1st day	1.153	1.171	0.018	1.56
15th day	1.153	1.182	0.029	2.51
30th day	1.153	1.195	0.042	3.64
45th day	1.153	1.209	0.056	4.86
60th day	1.153	1.215	0.062	5.38
75th day	1.153	1.226	0.073	6.33
90th day	1.153	1.234	0.081	7.03

Table 8: ZnO's percentage of swelling when put on a nano composite

Number of days	Weight at launch for a nano composite	Nano composite's total weight	Weigh differently	Percent swelling
1st day	0.743	0.744	0.001	0.13
15th day	0.743	0.745	0.002	0.26
30th day	0.743	0.747	0.004	0.54
45th day	0.743	0.748	0.005	0.67
60th day	0.743	0.750	0.007	0.94
75th day	0.743	0.751	0.008	1.08
90th day	0.743	0.754	0.011	1.48

4.0 Conclusion

In this study, zinc nitrate and sodium hydroxide are used as starting ingredients to create ZnO NPs utilising the co-precipitation method. An XRD analysis of the produced ZnO NPs revealed that nano-particle production had taken place. The existence of polyester, a hardener, and its interaction with ZnO NPs were demonstrated by FTIR analysis. For polyester nano composites with ZnO nano filler added, the sharpness and intensity differ. For the polyester system with ZnO addition, a small shift in the absorption bands is seen. This is brought on by ZnO NPs' high affinity to polyester. A thermo gravimetric analysis has been used to look at the thermal properties and how they degrade thermally. In comparison with pure polyester, the polyester/ZnO nano composites system's TGA thermogram displays reduced decomposition temperature characteristics. In comparison to pure polyester, the thermal stability was improved in nano-composite polyester/ZnO polymer materials. When compared to pure polyester, the polyester/ZnO Nano composite had a higher tensile strength, which suggests that there may have been an agglomeration of nano-particles due to a strong interaction with resin. When compared to a system made of pure polyester, ZnO-added polyester has a higher flexural strength. For the nano composites, the dielectric constant rises as the temperature rises. A reduced dielectric constant results from the orientation mode's inability to contribute to polarisation at low temperatures. The dielectric loss values rise gradually over 103 Hz after decreasing with frequency up to 1 kHz. This discovery is most likely the outcome of the system having a sizable number of nano-particles, which has an impact on the electrical conductivity mechanism present in the nano composites. The hydrophobic properties of the polyester/ZnO nano composites are higher than those of pure polyester.

5.0 References

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