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Sunflower Seed Husk As Green Agro-waste Filler For EPDM Rubber

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Abstract

Sunflower seed Husk (SSH) was used as green agro waste filler for EPDM matrix. Two particle sizes of SSH were used (91.8 µm and 7.5 µm). Chemical composition of SSH was investigated. The permittivity ε′and dielectric loss ε″ were measured over a frequency range 10^{-1} up to 10^{6} Hz for EPDM/WPS with two different particle sizes. Both values were found to increase by increasing SSH content. The curves relating dielectric loss ε″ and the applied frequency were analyzed into three relaxation processes and the obtained relaxations were interpreted. The dc conductivity σ was found to be in the order 10^{-15} S cm^{-1} which recommend such composites to be used in insulation purposes. Mechanical properties including tensile strength at break (σ_R) and elongation at break (ε_R) were found to decrease by increasing filler content.

Keywords: permittivity; polymer composites; thermal stability; sunflower seed husk

1. Introduction

For high-tech applications, Polymer compositions are an important process in improving properties of polymeric materials Natural fillers, for example, calcium Carbonates, mud, silica, hemp strands and wood filaments have been added to polymer composites demonstrating some alluring properties [1]. By further investigating the utilization of reused and waste natural fibers has become a significant way to resolve both resource shortage and environmental pollution as well. Additionally the collection of unmanaged squanders from the food business, especially in many nations is getting one of the environmental issues. Some plant processing byproduct have been attempted to produce composite material [2] rice husk, coconut shell, carrot powder, oil palm void organic product pack filaments, fish shell, grape particles, and sawdust, were utilized as a fillers to improve the tensile strength, flexibility modulus, and water ingestion [3]. Sunflower seed husks, a tremendous side-effect of the vegetable oil and food industry, could be utilized as harmless to the ecosystem filler [4]. Effect of Sunflower seed husks, as a filler, on mechanical properties, water absorption and fire stability upon polymer materials was studied [3-7]. But scarce information about its use as dielectric filler is available.

The processing temperature is the factor that determines the possibility of using a polymer as a Natural fiber composites matrix. This temperature should not exceed 190 °C as after that lignin may be thermally decomposes to basic elements [8]. EPDM rubber is a type of rubber synthesized from ethylene and propylene monomers (ethylene propylene copolymer) and on occasion with a measure of a third (diene) monomer (ethylene propylene diene polymers). EPDM has great versatility properties at low temperatures until about - 40 °C, likewise it is impervious to temperatures as high as 150 °C relying upon the evaluation and the relieving framework. Uncommon evaluations can even see higher temperatures [9]. EPDM is the overwhelming, and perhaps the solitary elastomer utilized today for thermoset material layers on account of its expansive scope of execution properties [10]. It is amazingly impervious to the components of outside openness, (Sunlight/UV openness, Water/Moisture and the Temperature limits related with overall environments

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(. The principle applications for EPDM are in the auto business for assembling segments like climate stripping, coolant hose, brake parts and in engine oil as a warmth stabilizer. [11]In the most recent many years, the fast improvement of elastic industry have prompted a broad utilization of such elastic materials and therefore various natural issues show up because of contamination, stockpiling, reusing and nursery impact [12].

In order to solve this problem this research work was directed towards the development of green biodegradable composites of rubber. For such reason, Sunflower seed Husk (SSH),without seeds, was implied to act as filler in the macro scale with two different particle size to EPDM in order to investigate its electrical as well as mechanical properties aiming to enhance it.

2. Experimental work

2.1 Materials

- Sunflower husks were purchased from a small project factory to extract oils, Cairo, Egypt**.**
- Ethylene propylene diene rubber (EPDM) was a white rubber- like solid and commercially known as Vistlon 7500 was obtained from Bayer AG, Germany.
- Peroxide (IPBP), 1,3 bis(isopropyl) benzene peroxide on calcium carbonate, having trade name of Perkadox 14140, with white color, molecular weight = 338 g=mol density = 1.5 g=cm3 was supplied by Aldrich company, Germany.
- Zinc oxide (ZnO) with specific gravity = 5.55–5.61, acidity (calc as SO3) = 0.4% maximum,weight loss at 150 ºC = 0.5% maximum and fineness = 99.8% through 3Smyth. C.P, 1998 mesh was supplied by Aldrich Company, Germany.
- N-cyclohexyl-2-benzothiazole sulphenamide (CBS) with specific gravity = 1.27–1.31, melting range = 95–100 ºC and pale gray powder was supplied by Aldrich Company, Germany

- .Tetramethyle thiuran disulphide (TMTD) with specific gravity = 1.29–1.31, melting point = 1485 ºC and order less powder was supplied by Aldrich Company, Germany.

- Naphthenic oil, with specific gravity at15 ºC= .94–.96, viscosity at 100ºC = 80–90 poise and deep green viscous oil was supplied by Aldrich Company, Germany.

2.2Preparation of - sunflower seed hull

Preparation of sunflower seed hull (SSH) The sunflower seeds were dehulld and the hull was dried in an air oven at 50 oC for 16 h. The dried sample was milled in a coffee grinder for about 8 min .The milled hull was then sired through a 60-mesh screen .The obtained sample was regrinding using 5 ML Zirconium oxide balls and zirconium oxide bowl volume 250 ML a PM 100 planetary Ball-mill(Retsch, Germany) as described by Zhu [13] with some modifications. Sample (150 g) was ground at 30Hz frequency for 60 min at room temperature (25ºC).

2.3.Chemical composition sunflower seed hull

Maisture, Protein (NX5.71), lipids, ash and crude fiber contents were determined according to AOAC [14]. Carbohydrates were calculated by difference according to the following equation **:**Total carbohydrates =100-(Protein+ fat+ash +fiber)

Table (1): Formulation of EPDM containing different concentrations of HSS , Ingredients in phr (part per hundred parts of rubber)

EPDM	100
Strearic acid	1
ZnO	5
Oil	7
CBS	1.25
TMTD	0.8
Peroxide (IPBP)	2
Filler (91.8 µm)	0-50 phr
Filler (7.5 µm)	0-20 phr

2.4.Composite Preparation

Composites were prepared on two rolls laboratory mill of outside diameter = 470 mm, working distance = 300 mm. The speed of the slow roll was 24 rpm with a gear ratio of 1:1.4. Different EPDM compositions were also prepared by incorporation with different WPS with two different particle size.

3. Techniques:

3.1.Transmissionelectron microscope(TEM)

Fillers were examined with a JEOL JX 1230 technique with microanalyzer electron probe. This technique was used to determine the particle size of the investigated fillers.

3.2. Scanning electron microscope.(SEM)

SEM was performed using a JXA-840A electron probe micro-analyzer (Jeol, Japan). The rubber specimen was broken in liquid nitrogen; the surface was then covered with a very thin layer of gold to avoid electrostatic charging during examination.

3.3.Thermogravimetric analysis (TGA)

TGA was performed using Perkin–Elmer, TGA7 (USA) instrument. The rate of heating was 10oC/min up to 800oC under nitrogen atmosphere.

3.4. Mechanical Properties

The stress-stain measurements were carried out at room temperature on a tensile testing machine, Zwick 1425, according to ASTM- D412- 06 (2006). The vulcanized sheets prepared for mechanical tests were cut into five individual dumbbell- shaped specimens by a steel die of constant width (4 mm). The thickness of the test specimen was determined by a gauge calibrated in hundredths of a millimeter.

A working part of size 15 mm was chosen for each test specimen. The mechanical properties (viz., stress and strain of the rubber compounds were determined according to standard methods using an electronic Zwick tensile testing machine, model 1425, in accordance with ASTM D 412-98, 2010.

3.5. Dielectric measurements

The dielectric properties were obtained using a computer-controlled impedance analyzer (Schlumberger Solartron 1260). The permittivity ε‘, loss factor tanδ and ac resistance Rac were measured at room temperatures ~ 30° C in a broad frequency range (0.1Hz -1MHz). The measurement was automated by interfacing the impedance analyzer with a personal computer through a GPIB cable IEE488. A commercial interfacing and automation software Lab VIEW was used for acquisition of data. The error in ε‘ and tanδ amounts to 1 % and 3 %, respectively. The temperature of the samples was controlled by a temperature regulator with Pt 100 sensor. The error in temperature measurements amounts 0.5° C. To avoid moisture, the samples were stored in desiccators in the presence of silica gel. Thereafter the sample was transferred to the measuring cell and left with P2O5 until the measurements were carried out. The reproducibility of the measurement was tested by re-measuring ε‘ and ε" after performing the experiment once again.

4. Results and Discussion:

4.1. Chemical composition of sunflower seed hull

Chemical composition of sunflower seed hull (SSH) are shown in Table(1) SSH was found to be characterized by the highest crude fiber , ash and carbohydrate (58.73, 4.63 and 30.74%) and lowest protein and fat(2.28 and 3.62%). Previously Dorrel and Vick[15] reported that the main organic macro-nutrients of sunflower seed hull (SSH) are Lipids (5%) carbohydrates (50%) and protein (4.0%), with the highest percentage of the content being in the lignin and cellulose-hemicellulose portion, with lignin comprising about 20-25% of the total weight**.**

Table (2):Chemical composition of sunflower seed hull(% on dry weight basis)

Constituents	%
Moisture	**2.85**
Protein	**2.28**
Fat	**3.62**
Ash	**4.63**
Crude fiber	**58.73**
Carbohydrates	**30.74**

4.2 .Scanning electron microscope (SEM)

Figure 1(a,b) present the morphologies of the soft and the coarse powder of investigated sunflower husk filler. From figure 1(a), the coarse sunflower husk is characterized by its huge part of enormous round and hollow grains, taking after short fibers. The cylindrical grains show relatively smooth surface with repeating parts that are highly ordered. The noticed longitudinal heading of fiber crumbling results from the construction of the sunflower husk which is normal for some kinds of vegetable fillers[12]. Figure 1(b) shows different morphology for soft particle size sunflower shells, for which less and smaller cylindrical grains were observed. As shown in SEM images, for soft sunflower husk powder the grain diameter is about 7.5µm, but for the coarse one, it is about 91.8 µm**.**

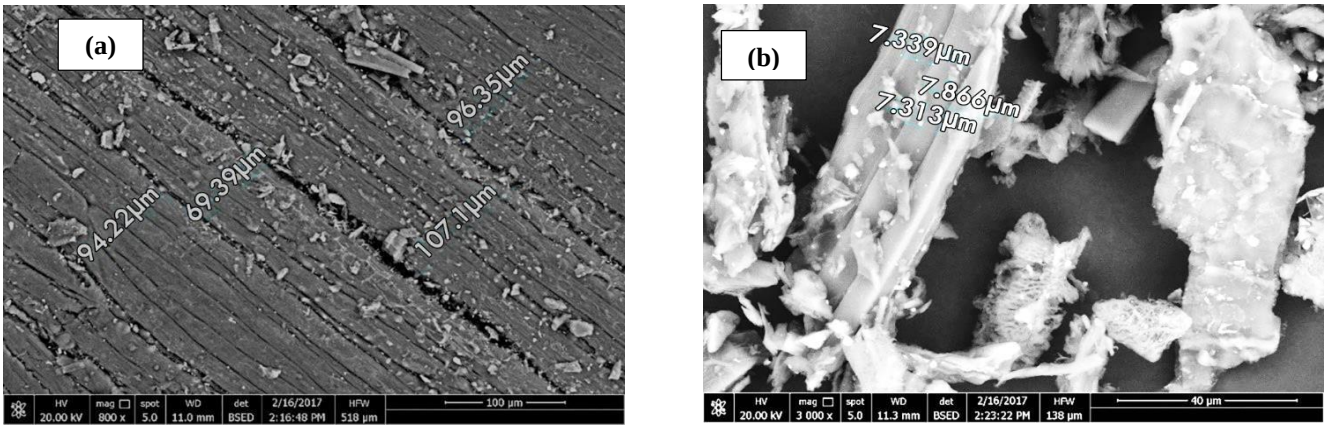


Figure 1(a,b) : present the morphologies of the coarse (a) and the softpowder (b) of investigated sunflower husk filler

In the SEM photographs of the natural fiber composites (NFC), presented in Fig. 2, empty spaces can be observed in the contact area between the hydrophobic matrix and the hydrophilic filler. Some of these voids were most likely formed during the preparation of the cross sections, which indicates the limited adhesion of the components. A portion of these voids were doubtlessly framed during the preparation of the cross areas, which demonstrates the restricted adhesion of the composite. Generally, these composites are described by a heterogeneous nature because of the heterogeneous nature caused by the irregular arrangement of the particles of filler [2]. The photographs in Fig. 2 (b,c) demonstrate also that NFC with coarse sunflower husk filler have weaker adhesion between its components compared to NFC with soft sunflower husk filler in Fig. 2 (d,e)**.**This referred to the formation of numerous voids on the surfaces of the samples' cross-sections.[7]. The number of voids in the composites increased as the filler content increased. Also, the porosity of the composites could be resulted from the restricted wetting conduct of the lopsided surface of the filler; then again, these voids maybe the main cause of composites mechanical properties deterioration. Additionally, it is expected that the ability of these composites to absorb a considerable amount of water would increase as the filler content increased [13].

4.3.Thermal gravimetric analysis (TG)

Thermal stability of pure EPDM and EPDM/ SSH composites with two different particle sizes of SSH filler were analyzed byTG technique. (TG) curves as well as differential TG curves (DTG), were given in Fig.3. From which it is seen that for EPDM a single-stage mass loss was detected.. The initial temperature where the loss of mass was found to begin is about 390oC. In the temperature range 390–500oCthe mass loss is about 76.3 %, resulting from thermal decomposition of the rubber [17]. This presumption was justified by the apparent of a peak in the same range on the DTG curve. Anyhow, above 500 OC the mass loss of is vanished and the mass remains virtually unchanged. In case of EPDM/ SSH composites ,Fig4a a new stage mass loss, at temperature range 255–360 °C, which is due to the degradation of hemicellulose and cellulose within sun flower seed shell [18].Table (3) illustrate the mass change at T=360 ºC (M360) with the filler loading (with particle size91.8µm and 5.7µm). From thistable it is clear that the loss of mass increases as the filler content increases but it decreases as the particle size decreases .For all investigated samples the T50 temperature, which corresponds to temperature at 50% initial weight remaining was found to be in the range of 464ºC(for EPDM) to 459ºC(for EPDM/15phr91.8µm SSH). So the difference between T_{50} temperatures could be negligible .From previous results, the addition of SSH doesn't have a significant negative impact upon thermal stability of EPDM matrix particularly with small particle size.

Table(3): remaining mass at decomposition temperature 360 ºC during decomposition of EPDM and its composites filled with 3,15phr coarse and soft HSS.

SSH content ,phr	M_{360}(%)
0	97.48
3 (91.8µm)	94.5
15(91.8µm)	86.34
3 (7.5µm)	95.257
15 (7.5µm)	90

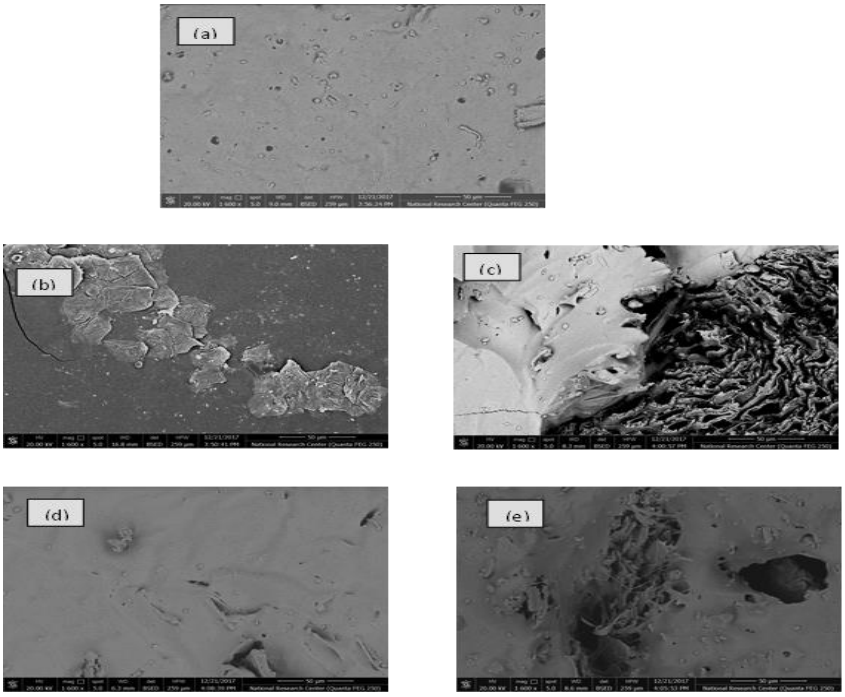


Figure 2(a-e): SEM images of EPDM/SSH composites (a) 0phr SSH, (b)10phr coarse HSS, (c) 40phrcoarse HSS ,(d) 3phr soft HSS and (e) 20phrsoft HSS.

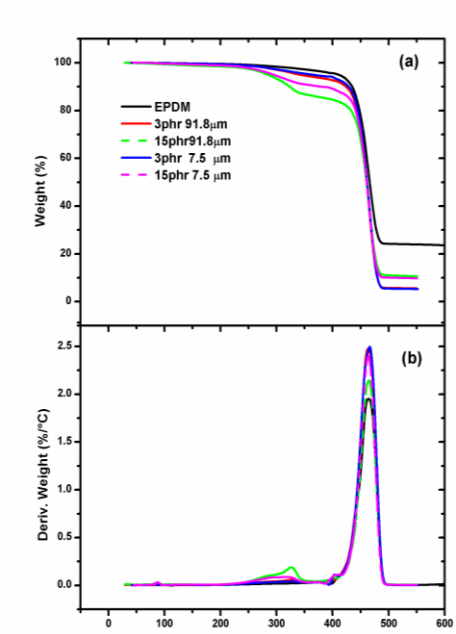
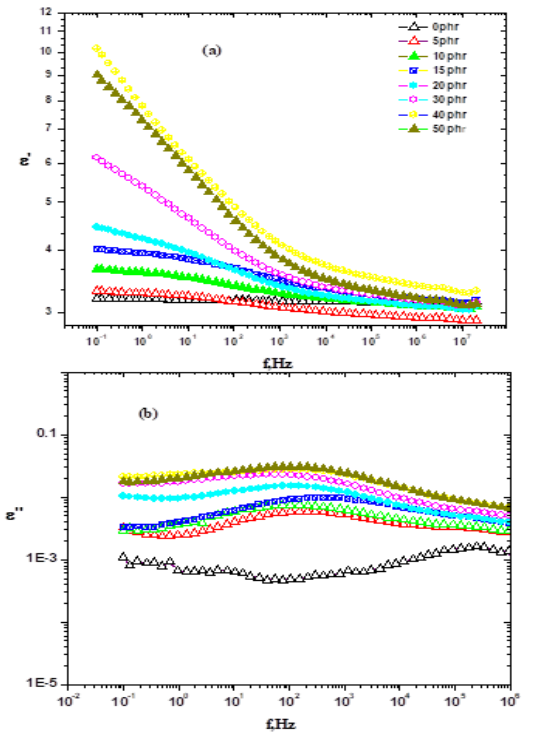


Figure 3 (a,b): FTG/DTG thermogram of EPDM and its composites filled with 3,15phrcoarse and soft HSS.



Figure(4): The permittivity and dielectric loss versus applied frequency at room temperature = 25°C for EPDM filled with SSH with average particle size = 91.8

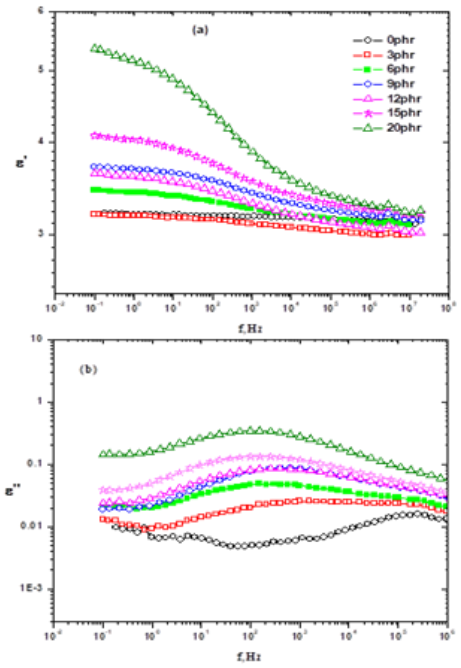


Figure (5) The permittivity ε' and dielectric loss ε" versus applied frequency at room temperature = 25°C for EPDM filled with SSH with average particle size= 7.5µm

4.4. Dielectric measurements

The permittivity and dielectric ε' and dielectric loss ε" were measured over a frequency range 10^{-1} up to 10^{6} Hz for EPDM/SSH with two different particle size (91.8&7.5µm).The obtained data were illustrated graphically in Figures (4&5) from which it can be seen that values of ε' decrease by increasing the applied frequency. This decrease shows anomalous phenomenon. This phenomenon is expected in most polymeric materials as a result of the fact that the rotational motion of the polar groups of the dielectric is not sufficiently rapid for reaching equilibrium with the applied field [19]. Reduction of the ε' values were expected in most polymeric mattresses [20]. This phenomenon is due to the fact that by increasing the applied frequency the dielectric relaxation involves the rotational dipolar polarization that depends upon the molecular structure of the material. At that high frequency range this rotational motion lags behind the electric field leading to decrease in ε' values [21]. Also it is seen that the values of ε' increase by increasing filler content. The significant increment in dielectric constant in hybrid composites with increase in fiber loading was due to the increment in interfacial as well as orientation polarizations accompanied by the presence of polar groups of cellulose in natural fibers [22].

This increase was found slightly higher for lower particle size which is logic due to the increase in the number of filler particles per unit volume by decreasing in particle size. The variation of the dielectric loss ε" with both the applied frequency and the percentage of filler were illustrated graphically in figures (4b&5b) which show that ε" values increase by increasing filler loading percentage **.**The curves relating the dielectric loss ε" and the applied frequency and presented in figures (4b&5b) were so complicated and broad indicating the presence of more than one relaxation process. For such reason, these curves were analyzed by using a computer program based on Fröhlich" and a "Havriliak Negami" functions. Three relaxation mechanisms were obtained in addition to the losses due to the electrical conductivity according to the equations given elsewhere [23]. Example of the analyses for EPDM/15 phr of SSH with average particle size = 91.8 µm is given in Figure (6).The first relaxation process which lies in the order of 0.4 s and 0.08 s for large and small particle size respectively was fitted by using Fröhlich function with distribution parameter P =3. This region ascribed either electrode polarization process or space charge injection which usually be the cause of high losses at the low frequency range [24]. It was interesting to find that the relaxation timeassociated with this reason does not affect by increasing the filler content with the two particle size under investigation.At higher frequency, another two relaxation processes were detected. The second one τ_2 with relaxation time in the order of 10^{-4} s was fitted by Havriliak Negami with parameters CC= 0.55 and CD = 0.8 respectively. The obtained values for τ_2 were illustrated graphically versus filler loading in Fig. (7) for the two particle size under investigation. This region attributed to the rotation of the side chain and found to increase by increasing the filler content. By increasing filler content, the rotating unites increase and consequently τ_2 values increase. Also it is seen that τ_2 values are higher in case of the lower particle size filler which is logic as the number of particles increase by decreasing the particle size .The third process τ_3 ascribe the movement of the groups attached to the side chain was analyzed by using Fröhlich function with distribution parameter P =3.This region was found to increase with the same manner that detected in case of τ_2.

The dc conductivity σ was calculated from the

measured ac conductivity and the data were included in Figure (8). From this Figure it is clear that σ values slightly increase by increasing both filler loading.In case of large particle size (91.8 μm) and after 20 phr loading an abrupt increase was noticed in σ values.

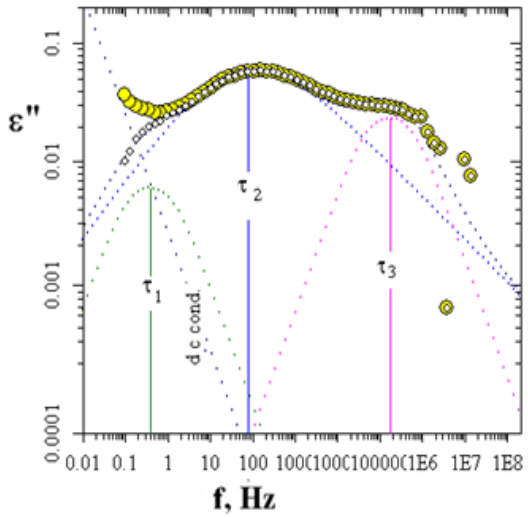


Figure (6): Example of analyses for EPDM/15 phr of SSH with average particle size = 91.8 μm

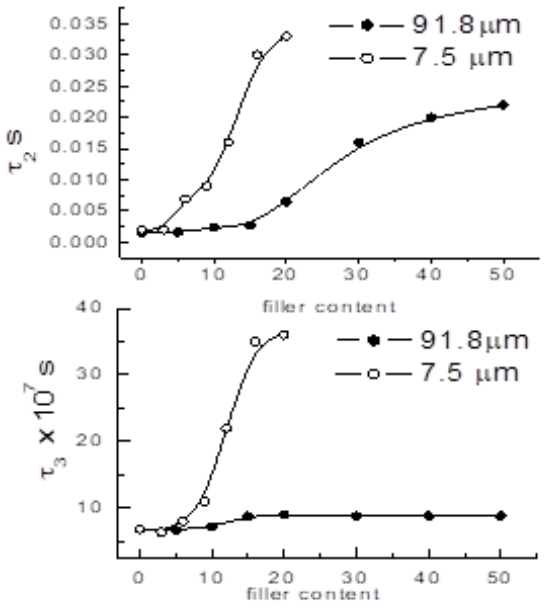


Figure (7): τ2 and τ3versus filler content

This increase was found to be in the same order 10^{-15} S cm^{-1}. This finding highly recommend such composites to be used in insulator purposes also it led to a conclusion that such filler as a green and renewable source could be used instead of the traditional fillers for EPDM.

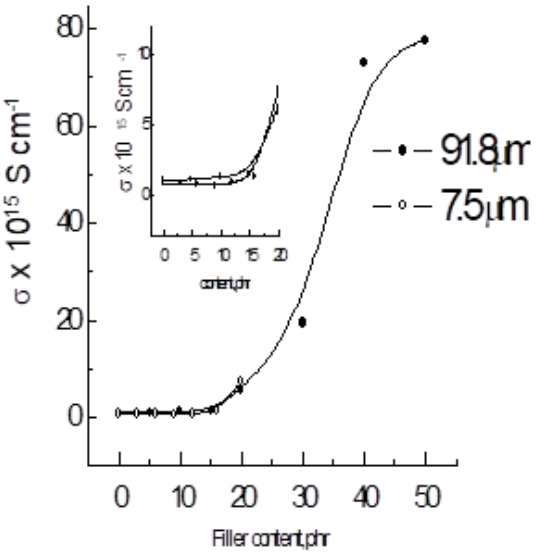


Figure (8): Electrical conductivity σ versus filler content

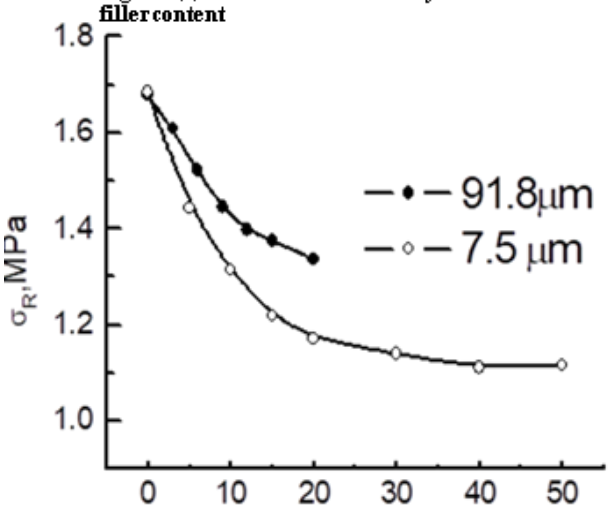


Figure (9) Tensile strength at break (σ_T) versus filler content, p

4.5. Mechanical Investigations

Mechanical properties including tensile strength at break (σ_R) and its elongation at break (ε_R) for the composites under investigation were investigated and the obtained data are given in Figures (9& 10).Figure (9) revels that the introducing of SSH as filler to EPDM matrix led to decrease in tensile strength at break (σ_R). This decrease is due to the incorporation of fiber into the matrix which led to disruption in the arrangement of rubber molecules

and consequently loss of the strain induced properties of the rubber matrix [25]. The elongation at break (ε_R) was measured and depicted in Figure (11) which show decrease in ε_R values with increasing filler content.This decrease may be explained in terms of the adherence of the SSH particles to the EPDM matrix which led to the stiffness of EPDM chain which cause the resistance to stretch when the strain is applied to it [25].

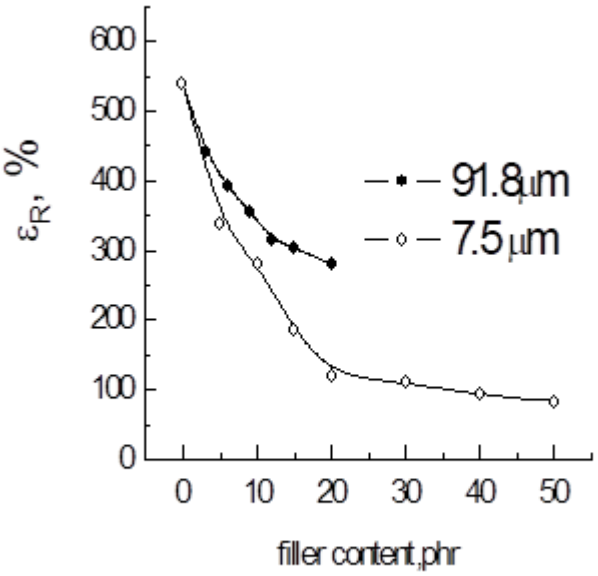


Fig. (10): Elongation at break (ε_R) versus filler content, phr

5. Conclusion:

From the above investigations it could be concluded that both permittivity ε′and dielectric loss ε″ values are enhanced by incorporation of WPS as filler into EPDM matrix. This enhancement was much more pronounced in case of lower particle size (7.5μm). Further, the dc conductivity σlies in the order 10^{-15} S cm^{-1} for all investigated composites which recommend it to be used in insulation purposes. The mechanical properties including tensile strength at break (σ_R) and elongation at break (ε_R) for the composites under investigation were found to decrease by increasing filler content. It is concluded that SSH filler as a green and renewable source could be used instead of the traditional fillers for EPDM.

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