ISSN : 0974 - 7486 Volume 11 Issue 11

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 11(11), 2014 [372-379]

Effect of rice husk ash and hydrated silica on the dielectric properties of LDPE composites

N.Samson Maria Louis*, ArjumanBanu, S.Sudha

Department of Chemistry, Sri Ramakrishna Institute of Technology, Pachapalayam, Coimbatore-641010, (INDIA)

E-mail : samsonmarialouis@yahoo.co.in

ABSTRACT

LDPE composites of rice husk ash (RHA) and hydrated silica at different filler concentrations were prepared and the dielectric properties were investigated. The optimum hydrated silica filled composite (30 parts/100 parts of LDPE) exhibits good dielectric constant and increased dielectric loss, which leads to the application as a good insulator. LDPE filled with RHA can be used as high frequency dielectrics due to low dielectric loss, resulted by the non-polar nature of RHA.

KEYWORDS

Polymeric composites;
Dielectrics;
Rice husk ash;
Hydrated silica;
Dielectric constant;
Dielectric loss.

INTRODUCTION

The dielectric polymer composites have attracted much interest due to their improved electrical properties in comparison with the polymeric materials that do not use fillers. Currently, various synthetic polymers are being prepared combined with several reinforcing fillers in order to improve the dielectric properties and obtain the characteristics demanded in actual applications (a). While considering the ability of a filler to improve the properties and cost effectiveness, waste materials have great importance. Among industrial, natural and agricultural wastes, the use of agricultural waste is of prime importance as they constitute the major waste of the world, namely rice husk and straw. Several studies are being conducted to find ways to use rice husk ash in place of synthetic fibers as reinforcing fillers. There is great demand for natural fillers, since the production of composites using natural substances as reinforcing fillers is not only inexpensive but also minimizes the environmental pollution by the characteristic biodegradability, enabling these composites to play an important role in rectifying future environmental problems (b-c). Ash derived from rice husk would have the properties of semi-reinforcing filler. Although carbonaceous in nature, it contains considerable silica in a hydrated amorphous form. The major ingredients of rice husk are 13-39% of ash, 34-44% of cellulose, 23-30% of lignin and 8-15% moisture. The ash content of rice husk is high enough to yield filler by burning away the organic fractions (d).

Low-density polyethylene (LDPE) is one of the thermoplastic material which exhibits good dielectric behavior and are widely used in dielectric insulation applications (e). Though LDPE is an insulator, our attempt was to improve the insulating property of LDPE by fillers like hydrated silica and rice husk ash, those are normally considered as major agricultural wastes. The dielectric parameters are imperative by themselves, but become more important when correlated to activity on a molecular level since chemical structure, polarity, and interaction of molecules decide the ability of dipoles to respond to electromagnetic field (f). This correlation allows investigation of the chemistry, flow and relaxations of polymers and composites which is again related to processing and morphology of polymer composites (g). Dielectric analysis is important in case of batteries, sensors, fuel cells, super capacitors and in the development of microelectronic packaging materials for performance optimization of high frequency devices (h).

In the present study, composites of LDPE with reinforcing fillers of rice husk ash (RHA) and hydrated silica were prepared and characterized. The important aim of this work is to explore the use of RHA as potential fillerderived from agro waste, in LDPE matrix for dielectric applications.

EXPERIMENTAL

Materials

LDPE (Grade NO WNC 71) was obtained from Indian Explosives Limited Howrah, West Bengal, India. Sodium hydroxide & concentrated hydrochloric acid were of commercial grade and obtained from Merck. RHA was obtained as gift sample from Molleswar Rice Mill, P.O.Mollarpur, Birbhum, West Bengal, India.

Synthesis of hydrated silica

100 g of RHA was taken in a 1000ml beaker and 20% 750ml sodium hydroxide solution was added to it. It was heated on a heating mantle at 100°C for half an hour and stirred continuously with a glass stirrer. After half an hour, the reaction mass was cooled to room temperature and filtered. Then it was heated upto 100°C with continuous vigorous stirring. 260ml of 12N hydrochloric acid was added drop wise to the hot solution. After the reaction was over, the reaction mixture was cooled to room temperature and washed thoroughly with water,filtered, dried at 130-140°C and weighed. Then it was ground in a grinding mill for 5 hrs to obtain hydrated silica.

Preparation of composites

Plastics composites were made in a Brabender Plastic order PLE 330. The beads form of LDPE was melted in a plasticorder using cam-type mixer with a rotor speed of 60 revolutions per minute and chamber temperature at 130°C. Then the fillers (RHA or hydrated silica) were added and the mixture was obtained within 3 min. Then, it was sheeted out in a two roll mill at 2.5mm nip setting. The sheeted out stock was compression molded at 130°C in a David Bridge single daylight electrically press having 30 × 30 cm platens.

Physical characterization

Bulk density

A measuring cylinder of 25 ml capacity having a uniform height and no pouring lip or deformation of the wall was taken and weighed. The sample was poured into the centre of the container from a height not more than 5 cm above the rim. The surface was leveled with a clean spatula and weighed. Bulk density was determined by the equation (1).

Bulk Density (g/ml)=Weight of the Sample(g) / Volume of the sample(ml) (1)

Specific gravity

The specific gravity bottle was first weighed without any sample. Then, it was half filled with the sample and weighed. The remaining space of the bottle was filled with distilled water, taking care that no air bubble was present and weighed again. Then, the specific gravity was determined by the following equation (2).

Specific gravity = Weight of the sample in air/ loss of weight in water (2)

Oil absorption

The sample was dried for 1 hr at 125°C and kept in a desiccator for 30 min.

1 g of the sample was taken on Whatmann filter paper and placed in a funnel. Dimethyl phthalate was taken in a burette and added very slowly to it. When it was completely absorbed, reading was taken. Oil absorption was found by equation (3).

Oil absorption (ml/g) = Volume of dimethyl phthalate(ml) (3)

Ash on ignition

The sample was dried at 125°C for 24 hr and 1 g of the sample was taken in a weighed silica crucible of 10 ml capacity and ignited in a furnace at 900 °C for 5 hr. Then it was allowed to cool to room temperature and weighed.

Ash on ignition (%) =weight of the ash ×100 (4)

pH

pH was found out by Systronics Expanded pH Meter 331 model.

Specific surface area

Quantasorb surface area analyzer was used for measuring the surface area of the fillers.

Sieve analysis

Test sieve B.S.S.410/43 of mesh size upto 240 were obtained from Geologists Syndicate Limited, Calcutta, West Bengal, India.

Dielectric properties

The dielectric constant and tan delta were measured with GR 716 C Bridge at room temperature. Experiments were done as a function of frequency and concentration of fillers.

RESULTS AND DISCUSSION

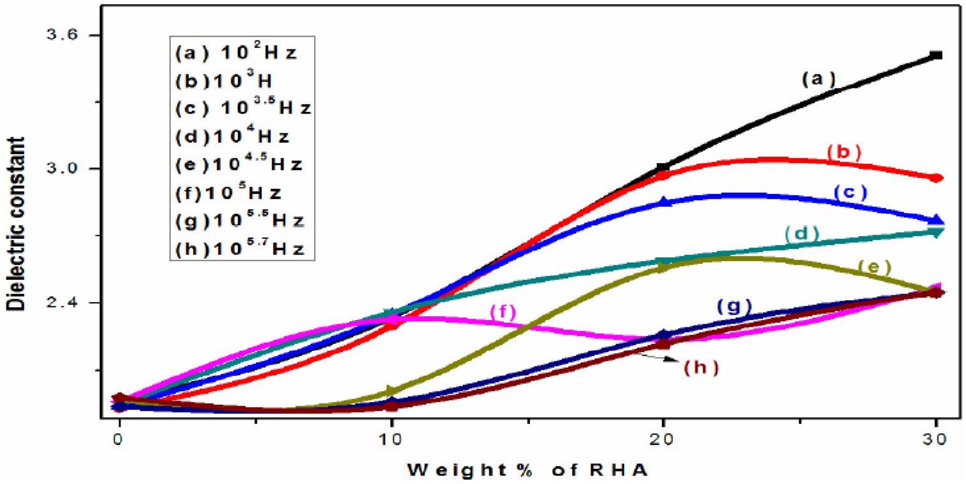
Physical properties like bulk density, specific gravity, oil absorption, ash on ignition, pH and specific surface area of the fillers were analyzed. From TABLE 1, it is obvious that RHA filler is gray in colordue to the presence of 10% carbon and hydrated silica is milky white due to the absence of carbon. From bulk density and specific gravity data, it is clear that RHA is denser than hydrated silica and from oil absorption and surface area data, hydrated silica is found to have better absorption compared to RHA. RHA is crystalline in nature whereas hydrated silica is amorphous (i). There is no significant change in pH. Data on ash on ignition show that RHA filler contains 90% silica with ignition loss 9-10% and hydrated silica contains 84-88% silica with ignition loss 10-15%. From sieve analysis, it was found that RHA is smaller than hydrated silica (a‘). All these physical properties put on light towards the inherent properties of the RHA and hydrated silica fillers.

Dependence of filler concentration on dielectric constant

Figure 1 shows the dielectric constant of polyeth-

TABLE 1 : Properties of the fillers

Sl. No	Properties	RHA	Hydrated silica
1.	Color	Gray	Milky white
2.	Bulk density (g/cm^3)	0.89	0.32
3.	Specific gravity	2.05	1.9
4.	Oil absorption (ml/g)	0.37	2.72
5.	Ash on ignition (%)	90.83	83.79
6.	pH	8.0	9.5
7.	Specific surface area (m^2/g)	90	337
8.	Sieve analysis(240 mesh) (%)	90	50

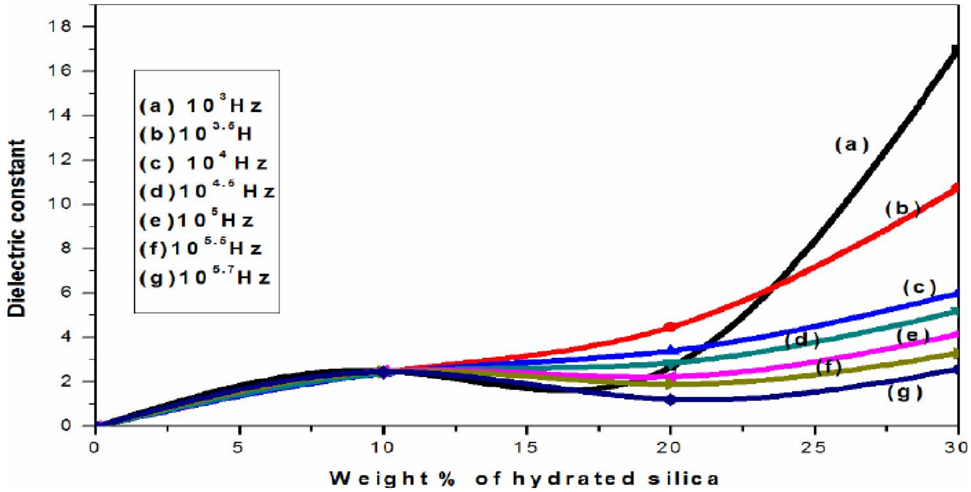


Plot of weight % of rice husk ash *vs* dielectric constant

Figure 1:Dependence of dielectric constant on rice husk ash concentration

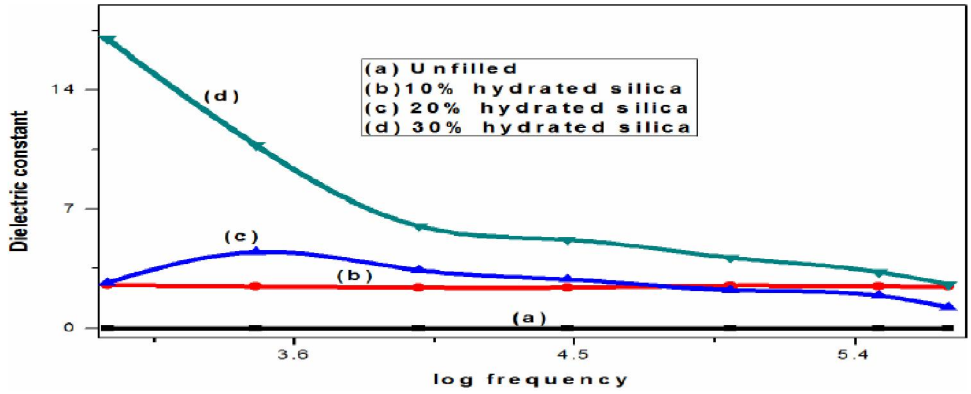
ylene composites as a function of RHA content at different frequencies. It can be seen that the dielectric constant marginally increases up to 10 weight percent of the filler loading. As the concentration of filler increases beyond 10 wt. percent, the property shows a large increase. In the case of RHA composites a leveling off is observed in all cases except at the very low frequency plot. Since, the individual dielectric constaof rice husk ask is higher than that of LDPE,it will influence the values of resultant properties of thecomposites (aa).

In general, when there is very low concentration of filler (Figure 1), the dielectric constant is low but when there is very high concentration of filler, the dielectric constant is found to increase. As the weight percentage of filler increases the space charge increases and it may lead to the polarization. This polarization will induce the polarization in polymeric matrix and thus the composites are having higher dielectric constant. Dielectric constant depends both on amount of filler as well as the frequency (ab). The composites show higher dielectric constant at lower frequencies. As the frequency increases molecular movements are arrested and this will lead to the decreased value of dielectric constant. The super-low frequency range is associated with Maxwell-Wagner interfacial polarization. Figure 2 also shows similar trends in the dielectric constant values of composites as a function of different weight percentage of hydrated silica at different frequencies. In this case also the dielectric constant increases up to 10 wt. % of filler for all the frequencies. After 10 wt. % there is a sharp increase and there is no leveling off of dielectric constant values. At higher loadings of hydrated silica filler the presence of OH groups may lead to the increased polarity. This enhances the polarization mechanism of the composites. As frequency is enough for introducing sufficient molecular movements and thus dipolar orien-



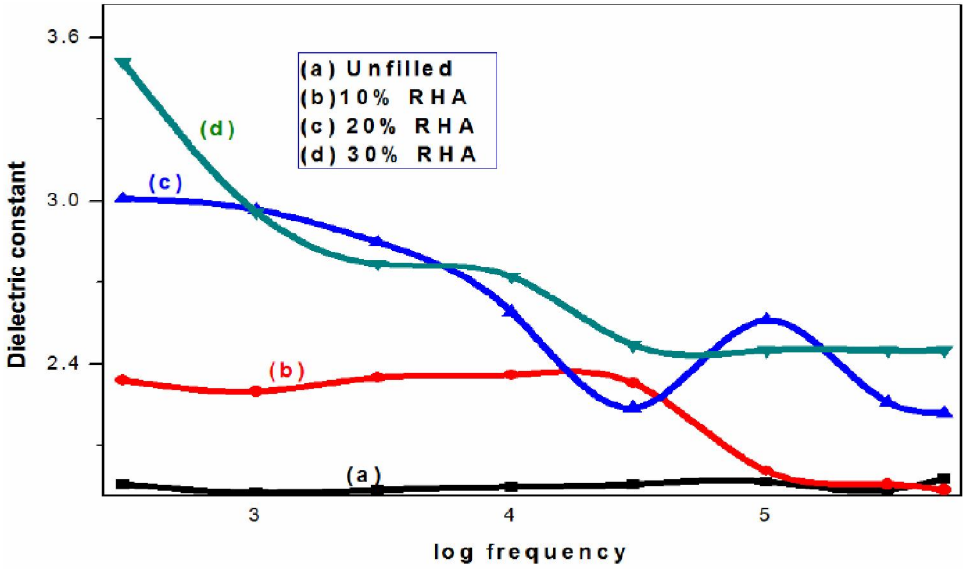
Plot of weight % of hydrated silica *vs* dielectric constant

Figure 2 : Dependence of dielectric constant on hydrated silica concentration



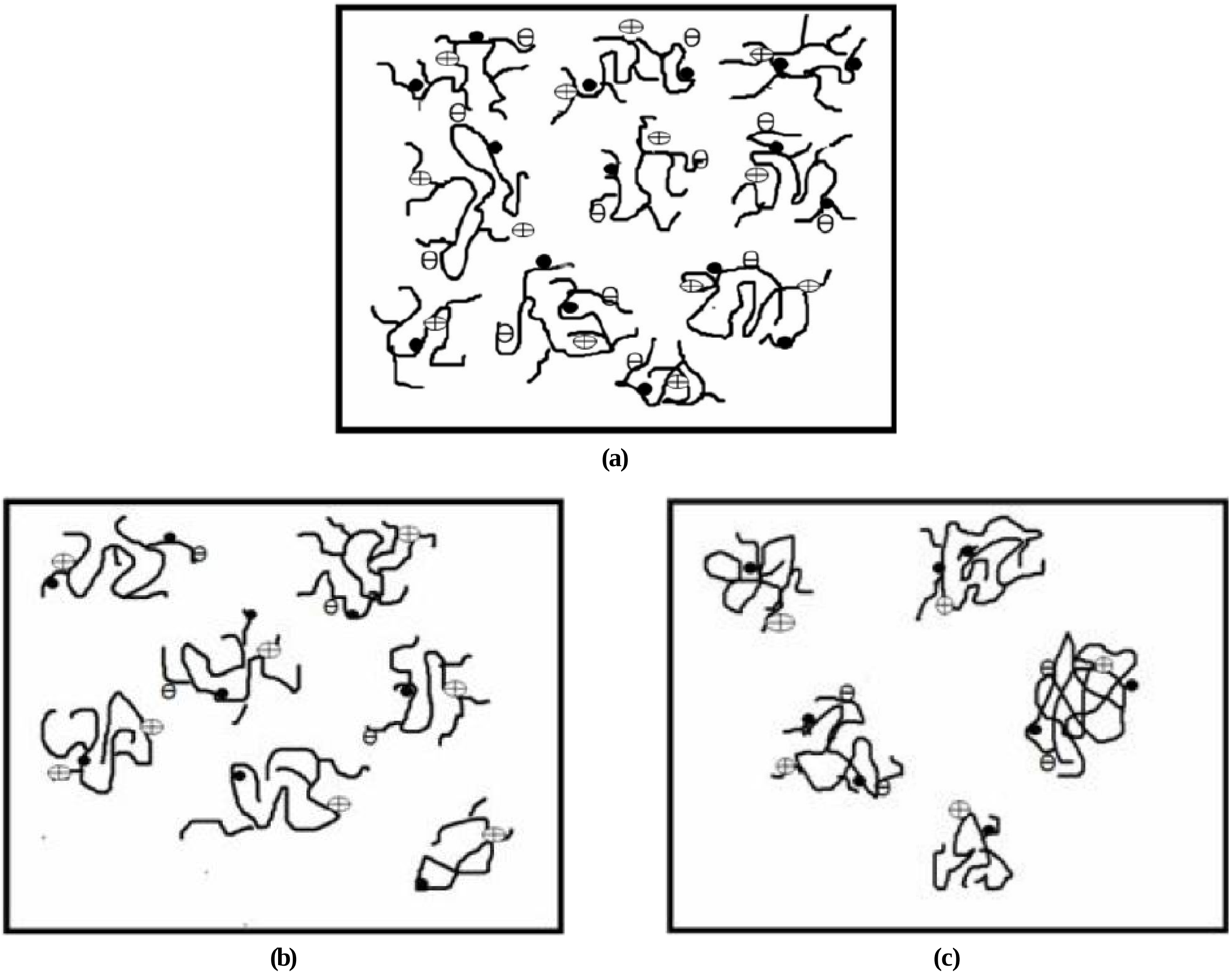
Plot of log frequency *vs* dielectric constant of hydrated silica

Figure 3 : Dependence of dielectric constant on frequency variation in PE/Hydrated silica composites



Plot of log frequency *vs* dielectric constant of rice husk ash

Figure 4 :Dependence of dielectric constant on frequency variation in PE/Rice husk ash composites


(a)

(b)

(c)

Schematic representation of dipolar orientation at low frequency(a), medium frequency(b), high frequency(c)

Figure 5: Schematic representation: Effect of frequency on dielectric constant

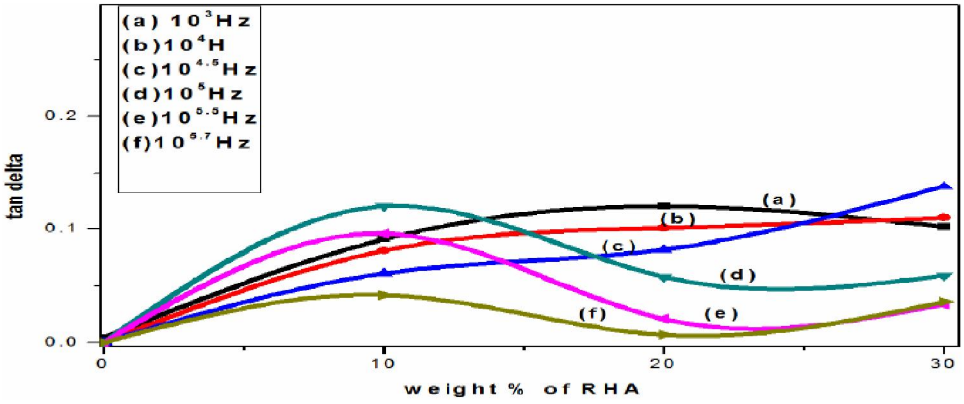
tation, dielectric constant value is increased (ac).

Frequency dependance

It can be seen from Figures 3 and 4 that the effective permittivityvalues of LDPE and their composites increase with decreasing frequency. Permittivity is a frequency dependent parameter in polymer systems. Dielectric constant of a polymer is determined by polarization of molecules. If molecules are highly polarised, the dielectric constant will be higher. The overall polarizability is contributed by atomic, electronic and orientation polarizations. Atomic or electronic polarizations are instantaneous and their effects are seen at higherfrequencies (ad). Dipole or orientation polarizations arise due to the presence of polar groups in the fibres. An electrical field will always displace the centre of charge of the electrons with respect to the nucleus and thus induce a dipole moment. In the case of orientation polarization, the material must have natural dipoles which can rotate freely. In thermal equilibrium, the dipoles will be randomly oriented and thus carry no net polarization. Interfacial polarizations arise as the composites are heterogeneous and their effects are seen mainly at low frequencies. In case of that polarization, surfaces, grain boundaries, interphase boundaries (polymer- filler) may be charged, i.e. they contain dipoles which may become oriented to some degree in an external field and thus contribute to the polarization of the material (ae). The fillers thus aid in increasing the polarisability of the composites. Also, the effective permittivity in composites is determined by dielectric polarization and relaxation mechanisms in the bulk of the composite material. In the present case, these are polarizations associated with LDPE as well as fillers and interfacial polarizations at the LDPE-filler interfaces.

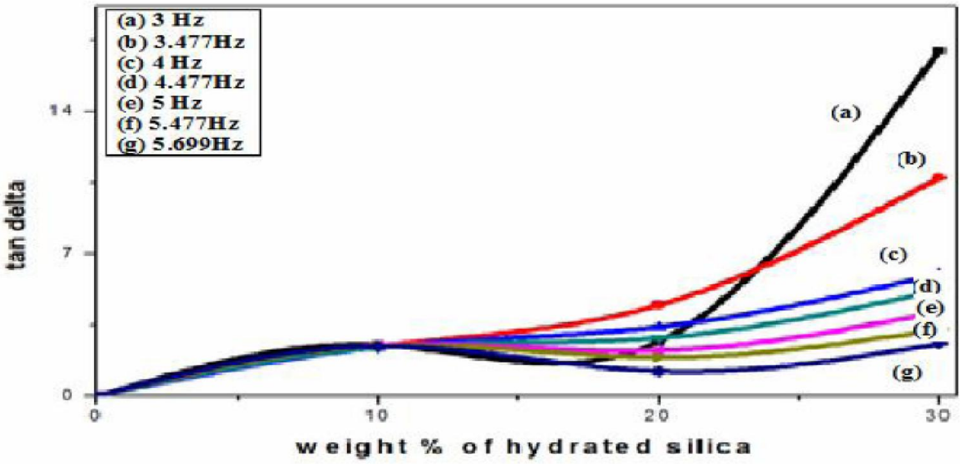
Since LDPE is a non-polar molecule, it has only atomic and electronic polarisation which is instantaneous. So, there is little variation in the dielectric constant with frequency (af). For LDPE/RHA composites or LDPE/ hydrated silica composites, the dielectric constant increases with filler content over the entire range of frequencies. The increase is higher for low frequency, lower for medium frequencies and very small for high frequencies. As shown in the schematic representation (Figure 5), the dipolar orientation occurs at lower frequency region due to the interaction between matrix and filler. As the frequency increases the point is reached when the dipole orientation cannot be completed in the time available.

In a typical LDPE system, the LDPE component of permittivity is governed by the number of orientable dipoles present in the system and their ability to orient under an applied electric field (ag-ah). Usually, the ethylene units, branch points and density in LDPE contribute to the dielectric relaxation mechanisms. At lower frequencies of applied voltage, all the free dipolar functional groups in the LDPE chain can orient themselves resulting in a higher permittivity value at these frequencies. As the electric field frequency increases, the bigger dipolar groups find it difficult to orient at the same phase as the alternating field, so the contributions of these dipolar groups to the permittivity goes on reducing resulting in a continuously decreasing permittivity of the LDPE system at higher frequencies. Similarly, the inherent permittivities in rice husk ash and silica particles also decrease with increasing frequencies of the



Plot of weight % of RHA *vs* tan delta

Figure 6 : Dependence of dielectric losson rice husk ash concentration



Plot of weight % of hydrated silica *vs* tan delta

Figure 7 : Dependence of dielectric lossonhydrated silica concentration

applied field. This combined decreasing effect of the permittivity for both LDPE and the filler particles result in a decrease in the effective permittivity of the LDPE composites, when the frequency of the applied field increases.

Tan delta measurements

The variations of tan delta in LDPE composites with RHA and silica, as fillers are presented in Figures 6 and 7 respectively. The tan delta value increases up to 10 wt % filler followed by decreasing and leveling off at higher concentrations. Tan delta depends on the electrical conductivity of the polymer composites. The electrical conductivity in turn depends on the number of charge carriers in the bulk of the material, the relaxation time of the charge carriers and the frequency of the applied electric field (ai). Since the measurement temperatures are maintained constant, their influence on the relaxation times of the charge carriers is neglected. Over the current frequency range of measurement, charge transport will be mainly dominated by lighter electronic species. Regarding dielectric properties of LDPE containing hydrated silica, there is a sharp increase in tan “ due to the presence of hydroxyl groups available for relaxation in the composites. Hydroxyl groups in hydrated silica exhibit quite high power loss at certain frequencies, the maximum power loss corresponding to this point of inflection in the curve. At very low frequencies, the dipole movements are able to keep in phase with change in dielectric field and power loss is low. As the frequency is increased the point is reached when the dipole orientation cannot be completed in the time available and the dipole becomes out of phase. After 10% hydrated silica in LDPE system, especially at lower frequency, there is a sharp increase in dielectric properties due to the interfacial polarization arising from difference between the conductivity of various phases. In these cases, loss can becharacterized by frequencies between 10^{-3} Hz to 10^{3} Hz, which may affect the electrical properties of materials in technical use. The geometry and distribution of the two phases are important as discussed bySillar (b`) The low frequency dielectric constant resulting from interfacial polarization can be several orders of magnitude larger than the value observed at high frequency. The higher frequency loss maximum was due to dipole orientations, the lower frequency maximum was shown to be due to interfacial polarization and the low frequency rising loss was due to D.C. conduction in the sample

CONCLUSION

LDPE/RHA and LDPE/hydrated silica composites were synthesized by melt mixing followed by compression moulding. LDPE containing hydrated silica can be used as an insulator due to its high dielectric constant and LDPE filled with RHA can be used as high frequency dielectrics due to the low dielectric loss. LDPE composite systems with inorganic fillers display someadvantageous dielectric behaviors. The permittivity and tan delta values in the composites are found to be lower than that of unfilled systems.

REFERENCES

[1] A.Baharin, H.G.B.Premalal, H.Ismail; A.Polymer Testing, **21**, 833 **(2002)**.

[2] H.Taek-Sung, L.Bum-Jae, P.Hee-Jun, S.Jungil, Y.Han-Seung, K.Hyun-Joong; Composite Structures, **63**, 305 **(2004)**.

[3] K.Dhirendra, D.Rashmi, S.P.Tambe, S.K.Singh, V.S.Raja; Surface and Coatings Technology, **205**, 5470 **(2011)**.

[4] R.Ciobanu, S.Aradoaei, R.Darie, M.G.Constantinescu; Journal of Non-Crystalline Solids, **356**, 768 **(2010)**.

[5] L.Jiayou, D.Yuan, L.Na, W.Yao, Z.Zhiwei, D.Yu; Materials Letters, **64**, 528 **(2010)**.

[6] Z.Wenying; ThermochimicaActa, **512**, 183 **(2011)**.

[7] X.Changsheng, T.Ying, X.Xianping, W.Yun; Contraception, **83**, 255 **(2011)**.

[8] J.González-Benito, F.Martínez, G.González-Gaitano; European Polymer Journal, **47**, 1495 **(2011)**.

[9] P.Sirilux, M.Supak; Polymer Testing, **30**, 716 **(2011)**.

[10] M.L.Rochel, M.Fabiano, C.C.M.Flávia; Desalination, **276**, 266 **(2011)**.

[11] C.R.G.Furtado, C.H.M.Da, Y.Visconte, R.C.R.Nunes; Journal of Applied Polymer Science, **83**, 2331 **(2002)**.

[12] V.V.R.Narasimha, V.Raja, A.K.Sharma; Mater Lett, **58**, 324 **(2004)**.

[13] B.Twombly, D.D.Shepard; ThermochimActa, **272**,125 **(1996)**.

[14] K.B.Ajit, N.M.L.Samson; Die AngewandteMakromolekulareChemie, **139**, 71 **(1986)**.

[15] K.Thein, N.Domasius; Technology & Engineering, **15**, 603 **(2008)**.

[16] T.R.M.Rama, S.Vishal, A.R.Kulkarni; Journal of Applied Polymer Science, **90**, 3602 **(2003)**.

[17] M.T.Joy, S.Santanu; IEEE Transactions on Dielectrics and Electrical Insulation, **17**, 15 **(2008)**.

[18] W.Akiyoshi, S.Takeshi, N.Haruki, U.Hatsuho; J.Phys.Chem., **93**, 357 **(1987)**.

[19] A.Eisenberg, G.Tsagaropoulos; Macromolecules, **28**, 6067 **(1995)**.

[20] L.Qianlong; Journal of Computational Physics, **230**, 8256 **(2011)**