Original Research Article

The Effect of ZnO nanoparticles Filler on Complex Permittivity of ZnO-PCL Nanocomposite at Microwave Frequency

Abstract

ZnO Nanoparticle was succesfully prepared by microwave irradiation method. The nano particles were then used as filler in the ZnO-PCL nanocomposites. The composites were prepared via the melt blend technique. The effect of the different percentages of the ZnO nanoparticles filler on the complex permittivity of the ZnO-PCL nanocomposite was investigated using the magnitudes of the reflection coefficient from the open ended coaxial sensors to determine complex permittivity of a sample under test. The different percentages used are 25%, 35%, 45%, 50%, and 70% ZnO nano fillers. The result from the measurement showed that the nano filler significantly affected the value of the complex permittivity of the ZnO-PCL nanocomposites. Amongst other observations, its was found that the dielectric constant of the material under test (MUT) increases as the filler content increases. The result also showed that the dielectric constant at 8 GHz is higher than the dielectric constant at 12 GHz for all samples used. Measurement result showed that the 70% ZnO nano filler produced a mean complex permittivity of (ε_r=4.07-j0.71).

Keywords: nanocomposites, nanoparticles, open ended coaxial probe, complex permittivity.

Introduction

An open ended coaxial line has been used by many researchers for measuring the complex permittivity of liquid materials and semi-liquid materials non-destructively (Faiz et al, 2012; Poumaropoulos et al, 1993). Most of the researches have reported only on the dielectric constant especially for liquid materials. The determination of complex permittivity of solid material using the open ended coaxial probe has not been investigated in addition to the effect of different percentages of filler compositions in host matrix. In this paper, zinc oxide-polycaprolactone (ZnO-PCL) nanocomposites were prepared via microwave irradiation and melt blend techniques. The prepared material are then investigated for their complex permittivity using the open ended coaxial probe technique. Details of the preparation method of the composites is not discussed in this work, however, detailed discussion on the measurement technique as its affect complex permittivity when changing the percentage of the filler content in the matrix is presented.

The technique involves placing the sample flat against an open end of a coaxial probe, where its reflection coefficient is measured from the interaction of the propagating wave and sample. The open ended probe consist of a coaxial line having inner and outer radii a, and b, respectively, filled with a lossless homogeneous dielectric (PTFE) having a relative permittivity that is terminated in the z-plane, onto a flat metallic flange extending theoretically to infinity in the transverse direction where, $z = 0$ (Jusoh, et al, 2011). The material at the end of the coax opening is assumed to be homogeneous, isotropic, linear, and nonmagnetic, and having complex permittivity extending to infinity. The schematic diagram of an open ended coaxial sensor with a sample, Agilent 85070B dielectric probe, and shorting block are shown in Figs.1a and 1b.The OEC technique has been successful in the measurement of complex permittivity of liquid and semi-liquid materials as reported in literatures. Hassan, et al (1997), successfully used to the OEC to measure moisture content of latex, Yeow et al, (2010) also used the open ended coaxial technique to measure the complex permittivity of oil palm fruit while Jusoh et al, (2011), measured the moisture content and complex permittivity of maize and kernel using OEC with high accuracy. However, none of the researchers measured the complex permittivity of a solid material involving changes in filler composition.

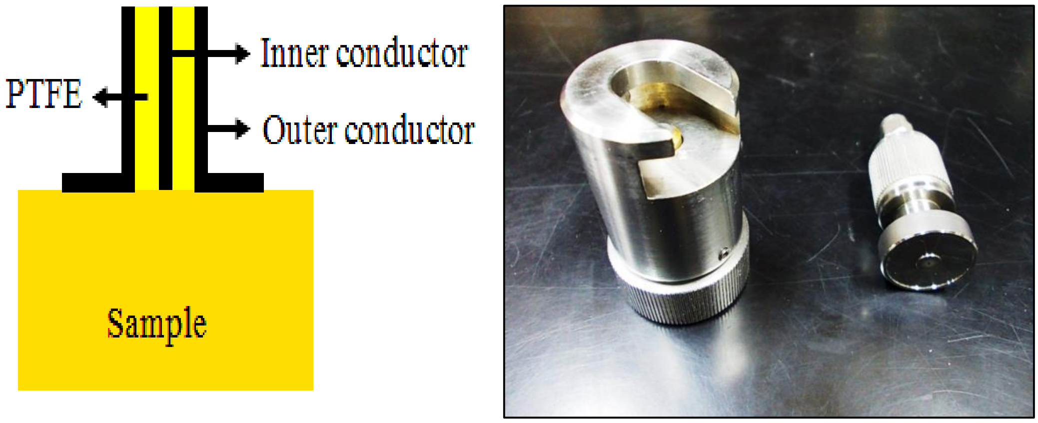

Figure 1: (a) Schematic probe and sample (b) Agilent 85070B dielectric probe (right) and the shorting block (left)

Theory

As stated earlier, the open ended probe technique is based on reflection coefficient measurement alone. The extraction of complex permittivity from the reflection coefficient is obtained from the equations below (Kim et al, 2013). The reflection coefficient, Γ, of the open ended coaxial sensor, the characteristic impedance, Z_0, of the measurement system and the complex permittivity, ε_r, of the material under test are related by;

$$\Gamma_r = \Gamma e^{j\varphi} = \frac{1 - jwZ_0\left[C(\varepsilon_r) + C_f\right]}{1 + jwZ_0\left[C(\varepsilon_r) + C_f\right]} \qquad (1)$$

Where, $C(\varepsilon_r) = C_0\varepsilon_r$, and C_0 is the capacitance of the capacitor filled with air, C_f is the capacitance independent of the material, and w, is the angular frequency. The values of C_0 and C_f are deduced by calibrating the open ended sensor with a standard sample of known dielectric permittivity, such as deionized water (Gannouchi et al, 1989).

Equation (1) after mathematical simplification will give:

$$\Gamma_r = \Gamma' + j\Gamma'' = \frac{1 - jwZ_0\left[C_0(\varepsilon' + j\varepsilon'') + C_f\right]}{1 + jwZ_0\left[C_0(\varepsilon' + j\varepsilon'') + C_f\right]} \qquad (2)$$

Where, the real and imaginary parts of complex reflection coefficient, Γ_r, are expressed as:

$$\Gamma' = \frac{1 + \Gamma'' w Z_0 C_0 \varepsilon' + w Z_0 C_0 \varepsilon'' + \Gamma'' w Z_0 C_f}{1 - w Z_0 C_0 \varepsilon''} \quad (3)$$

$$\Gamma'' = \frac{(1 + \Gamma')\left(w Z_0 C_0 \varepsilon' + w Z_0 C_f\right)}{w Z_0 C_0 \varepsilon'' - 1} \quad (4)$$

The complex permittivity, ($\mathcal{E}_r$= $\mathcal{E}$'-j$\mathcal{E}$''), can be deduced from equation (2), Simplifying the equation will give;

$$\varepsilon_r = \frac{1 - \Gamma_r}{j w Z_0 C_0 (1 - \Gamma_r)} - \frac{C_f}{C_0} \quad (5)$$

The real part of permittivity is calculated using the formula,

$$\varepsilon' = \frac{-2\Gamma''}{w Z_0 C_0 (|\Gamma|^2 + 2\Gamma' + 1)} - \frac{C_f}{C_0} \quad (6)$$

For the imaginary part pf permittivity, the value can be deduced by using the formula;

$$\varepsilon'' = \frac{|\Gamma|^2 - 1}{w Z_0 C_0 (|\Gamma|^2 + 2\Gamma' + 1)} \quad (7)$$

Method

The measurement set-up for the complex permittivity of ZnO-PCL nanocomposites pellets includes Agilent 85070B dielectric probe kit, a sensor probe, a mounting bracket, a cable, a 3.5 inch high density shorting block for calibration, adapters and a software for data collection and plotting. The network analyzer model used was the Agilent PNA-L N5230A, a retort stand was used to support the sensor during the measurement. The calibration for the complex permittivity measurement was performed using the OPEN SHORT LOAD Calibration Module. Figure 2 shows the experimental setup as used in this paper for the measurement of complex permittivity of different % ZnO-PCL nanocomposites pellets.

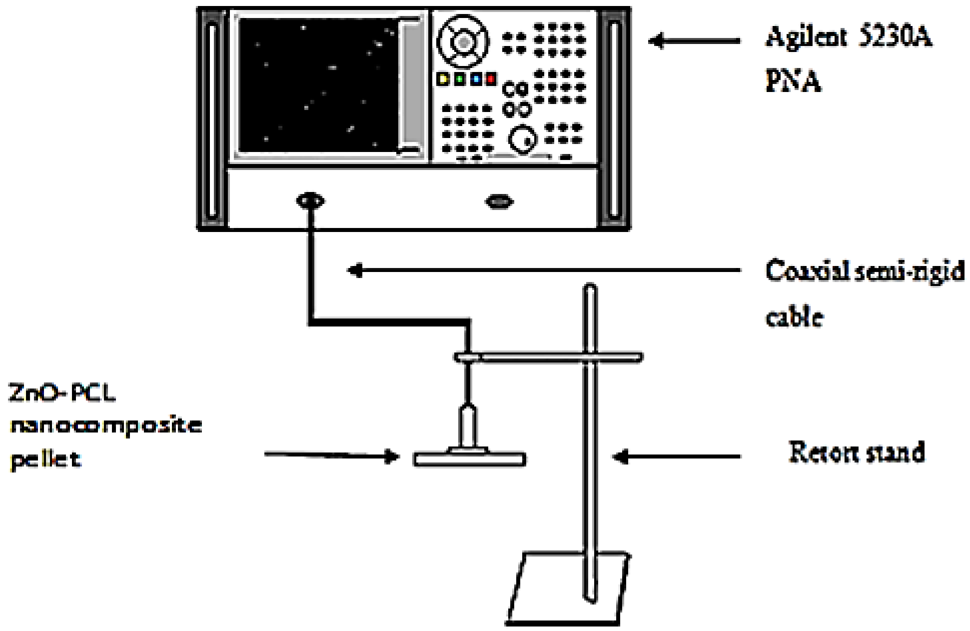

Figure 2: Complex permittivity measurement set-up

Following the manufacturer's recommended procedure, PTFE was measured as standard material. The measurement result for the PTFE sample was 2.01 for the dielectric constant, e' and the loss factor, e'' measured is 0.003 at X-Band (8-12 GHz). The complex permittivity thus measured is $\varepsilon_r = 2.01-j0.003$, which is in agreement with manufacturers value. Result of the PTFE measurement is shown in Figure 3.

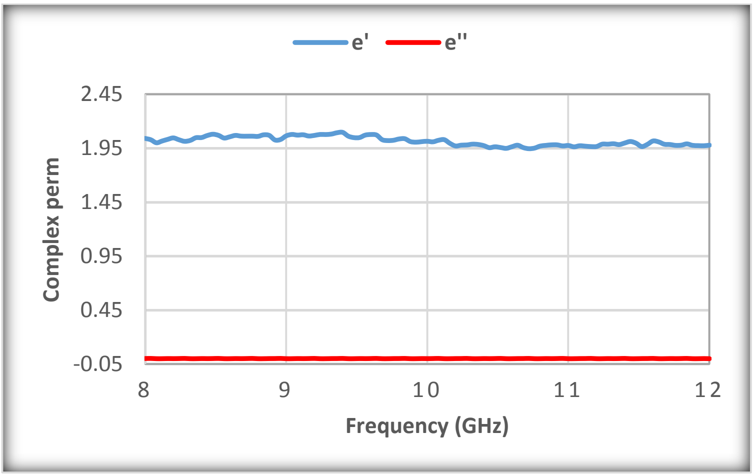

Figure 3: Complex permittivityfor PTFE at X-Band

After the successful measurement of the PTFE samples, the authors proceeded to measuring the different percentages of ZnO-PCL nanocomposites as tabulated in Table 1. ZnO-PCL nanocomposites were fabricated into pellets of same dimension with different ZnO percentage inclusion. The length and breadth of the pellets are 6.0 cm by 3.6 cm and a thickness of 8 mm each. These dimensions were chosen so as to cover the entire circumference of the probe so as to avoid any scattering of radiation at the edges of the probe. For efficient measurement, the manufacturer recommended minimum thickness when using the Agilent 85070B open ended coaxial probe is 8 mm (Agilent Technical Overview, 2012). Sample thicknesses below 8 mm thickness is prone to uncertainties in dielectric measurement due to the effect of multiple reflections in thinner samples.

Five different composition of ZnO-PCL nanocomposite were prepared via the microwave and melt blending method as stated earlier. For easy identification of the composites, they are labeled ZnO/PCL 25%, ZnO/PCL 35%, ZnO/PCL 45%, ZnO/PCL 50%, and ZnO/PCL 70%.

The variation in complex permittivity values of the different % ZnO-PCL nanocomposites samples against frequency in the range of 8 – 12 GHz are shown in Figure 4, 5 and 6 for the dielectric constant, loss factor and loss tangent respectively.

Table 1: Composition of raw materials used in composite preparation

ZnO powder		PCL pellets		
Weight (%)	Mass (g)	Weight (%)	Mass (g)	**Total mass (g)**
25.0	10.0	75.0	30.0	40.0
35.0	14.0	65.0	26.0	40.0
45.0	18.0	55.0	22.0	40.0
50.0	20.0	50.0	20.0	40.0
70.0	28.0	30.0	12.0	40.0

Result and Discussion

Careful observation on Figure 4 revealed that the value of dielectric constant is smaller for the composites with lower content of ZnO nanoparticles. However, further increase in ZnO nano content increases the dielectric constant of the composite. According to the effective medium theory (Bikky et al, 2010), the complex permittivity of polymer-based composite can be increased by adding fillers with higher permittivity values.The particle size of ZnO is the main parameter that has great influence on the dielectric activity. Decreased particle size increases the ZnO specific surface area, thus enabling good contact between the crosslinking agent particles and the polymer chains (Przybyszewska and Zaborski, 2009).

Sheen et al, (2011), reported using cavity perturbation method in the measurement of dielectric constant of TiO_2 samples. Their result showed an increase in the dielectric constant of TiO_2 sample with gradual increment of CaTiO3 or SrTiO3 components.

The two main dielectric polarization mechanisms which are contributing to the enhanced dielectric behaviour of the composites are rotation direction polarization (RDP) process and space charge polarization (SCP) process. It is reported that both RDP and SCP processes are contributing to the enhancement of dielectric response of the ZnO nanofillers (Lanje et al, 2013).

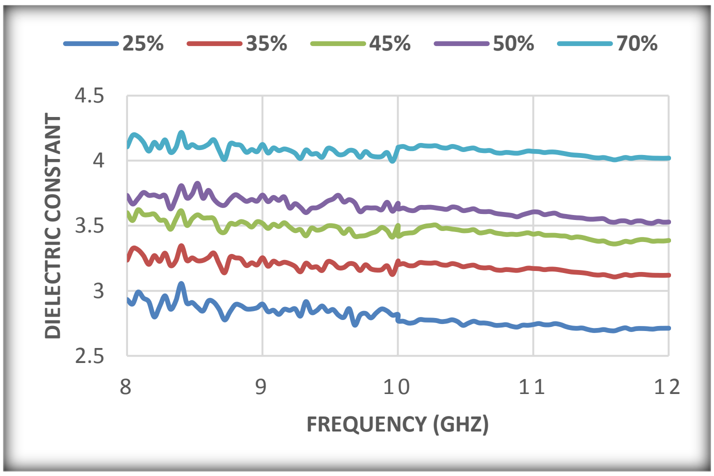

Figure 4: Variation in dielectric constant of ZnO-PCL nanocomposites

The ripple like nature of the dielectric constant at frequency range between 8 – 10 GHz are attributed to the effect of multiple reflection between the coaxial line and the surface of the sample under test. In addition, careful treatment, such as, calibration of the probe system, might also lead to the ripples shown at lower part of the X-Band frequency (Qiu et al, 2009).

Among other observation, the 50% filler showed that at 8 GHz, the dielectric constant is 3.73 corresponding to a loss factor of 0.59. The recorded dielectric constant for the 50% filler at 12 GHz is 3.52 corresponding to a loss factor of 0.57. Whilst the 70% ZnO nanofiller, the dielectric constant is 4.11 at 8 GHz corresponding to a loss factor of 0.71. The difference in the dielectric constant for the 70% ZnO nanofiller from the start point to end point is 0.09. Generally, there was an increase in dielectric constant as filler content increases whereas the dielectric constant decreases as the frequency increases. The decrease in dielectric constant as frequency increases is attributed to polarisation effect (Lian et al, 1995).

Further observation on Figure 5, suggest that ZnO nanofiller can change the property of the composites from a medium loss material to a dispersive material high loss material due to the high loss property of the ZnO nanofiller.

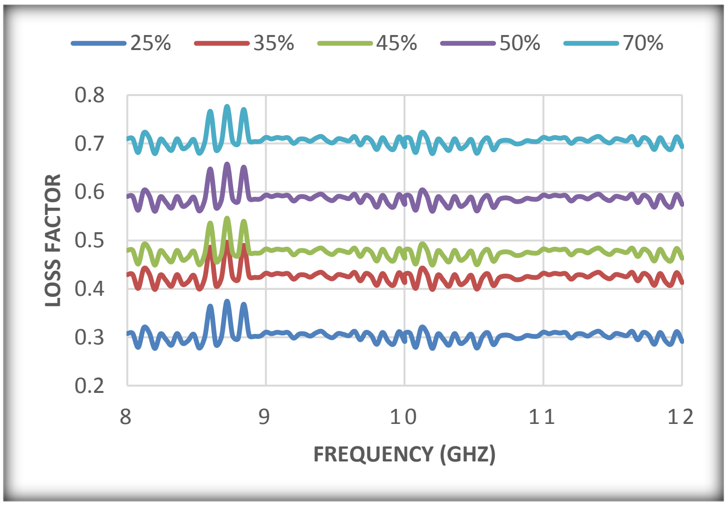

Figure 5: Variation in Loss factor of ZnO-PCL nanocomposites

Jablonski, (1978), reported that medium loss materials have loss factor from 0.05 to 0.2, whilst high loss materials have loss factor values above 0.3.

Thus, an increase of 35% ZnO nanofiller into the host matrix was found to quickly declassify the PCL from medium loss material to high loss material which is very suitable for radiation absorption at microwave frequency.

Figure 6 is the variation of the loss tangent for the different % ZnO-PCL nanocomposites. The loss tangent is the ratio of the loss factor to the dielectric constant. The loss tangent for all samples used in this study are calculated from the values given in Table 1 using the formula in equation (8);

$$tan\delta = \frac{loss\ factor}{dielectric\ constant} = \frac{\varepsilon''}{\varepsilon'} \tag{8}$$

The result in Figure 6, clearly shows the declassification of PCL from a low loss material to a high loss material from the value of the 70% ZnO nanofiller. The mean value is 0.16 which magnitude is greater than 0.1, the value for low loss material.

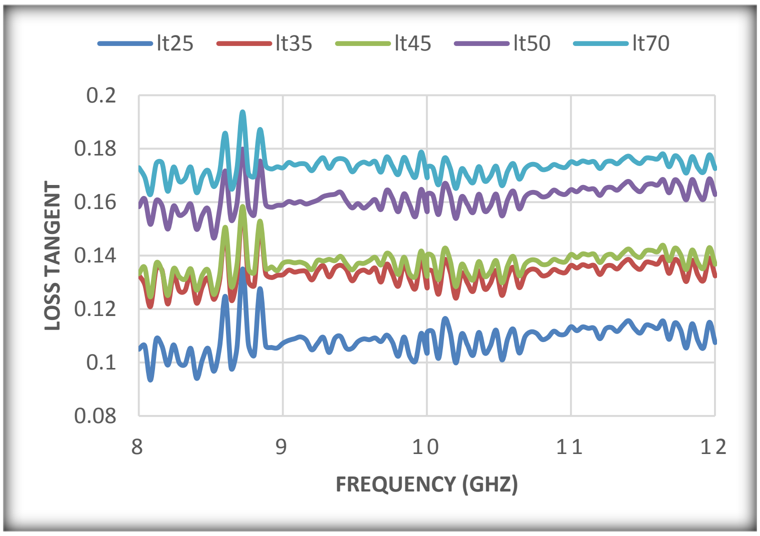

Figure 6: Loss tangent of all samples measured with OEC

Shown in Table 2, is the summary of the mean complex permittivity for the different % ZnO-PCL nanocomposites.

Table 2: Mean complex permittivity for all samples

Sample	$\varepsilon_r = \varepsilon' - j\varepsilon''$
PTFE	2.01-j0.003
ZnO/PCL-25%ZnO	2.79-j0.30
ZnO/PCL-35%ZnO	3.18-j0.42
ZnO/PCL-45%ZnO	3.46-j0.47
ZnO/PCL-50%ZnO	3.63-j0.59
ZnO/PCL-70%ZnO	4.07-j0.71

Conclusion

It is found that the open-ended coaxial technique provides alternative method to determine complex permittivity of solid materials by using the magnitude of reflection coefficient and phase measured. It is also shown that the complex permittivity of ZnO-PCL nanocomposites is significantly affected by the amount of filler inclusion in the composite. The OEC measurement technique is good for estimating complex permittivity of solid materials based on the results obtained for the ZnO-PCL nanocomposites. The overall result showed that the ZnO-PCL nanocomposites with the highest ZnO nanoparticle filler had the highest magnitude of dielectric constant and loss factor. Result also confirmed that the dielectric constant decreased with increasing frequency due to polarization effect.

REFERENCES

Agilent Technology Overview, (2012). Fundamentals of RF and Microwave Power Measurements (Part 3), Power Measurement Uncertainty. USA

Bikky, R., Badi, N., &Bensaoula, A. (2010). Effective Medium Theory of Nano dielectrics for Embedded Energy Storage Capacitors. *Proceedings of the COMSOL Conference*, Boston.

Faiz, M. Z. (2013), *Design and analysis of monopole sensor for the determination of moisture content in dioscoreahispida tuber*, PhD Thesis, Universiti Putra, Malaysia.

Ghannouchi, F. M., R. G. Bosisio, Y. Demers, and R. Guay, (1989), Computer aided measurement of dielectric properties of salinesolutions using a six-port reflectometer," *IEEE Trans. Instrum.Meas.*, Vol. 38, No. 2, 505-508

Hassan, J. Khaida, K, and Wan Yusoff, W. M. (1997), Microwave Dielectric Properties of Hevea Rubber Latex in the Temperature Range of -30°C to 50°C. *Pertanika Journal of Sci. & Techno*. 5(2): 179-190

Jablonski, D. (1978), "Attenuation characteristics of circular dielectric waveguide at millimetre wavelengths," *IEEE Transactions onMicrowave Theory and Techniques*, Vol. 26, no. 9, pp. 667–671,1978.

Jusoh, M. A, Abbas, Z. Hassan, J. Azmi, B. Z and Ahmad, A. F. (2011), A Simple Procedure to Determine Complex Permittivity of Moist Materials Using Standard Commercial Coaxial Sensor, *Measurement Science Review*, Volume 11, No. 1

Kim Y. L, Boon, K. C, Abbas, Z, Kok, Y. Y, and EeMeng, C, (2013), Amplitude-only measurements of a dualopen ended coaxial sensor system for determination of complex permittivity of materials, *Progress In Electromagnetics Research M, Vol. 28, 27-39*

Lanje, A. S. Sharma, S. J. Ningthoujam, R. S. Ahn, J. S. Pode, R. B. (2013). Low temperature dielectric studies of zinc oxide (ZnO) nanoparticles prepared by precipitation method, *Advanced Powder Technology*, 24, 331–335

Lian, A. Besner, S and Dao, L. (1995). "Broadband dielectric and conducting properties of poly (N-alkylanilines)," *Synthetic Metals*, Vol. 74, no. 1, pp. 21–27

Poumaropoulos, C., Misra, D. (1993). A study on the coaxial aperture electromagnetic sensor and its application in material characterization. In IEEE Instrumentation and Measurement Technology Conference, 18-20, 52-55

Przybyszewska, M. and Zaborski, M. (2009). The effect of zinc oxide nanoparticle morphology on activity in crosslinking of carboxylated nitrile elastomer, *eXPRESS Polymer Letters*, Vol.3, No.9, 542–552

Qiu, Z, Li, X &Jiang, W (2009). On Stability of Formulation of Open-Ended Coaxial Probe for Measurementof Electromagnetic Properties of Finite-Thickness Materials, *Journal of Electromagnetic Waves and Applications*, 23:4,501-511, DOI: 10.1163/156939309787612347

Sheen, J, Li, C. Y &Lin, S. W (2011) Measurements of MicrowaveDielectric Properties of $(_{1-x})TiO_2$. $_xCaTiO_3$ and $_{(1-x)}TiO_2$. $_xSrTiO_3$ thin Films by TheCavity Perturbation Method, *Journal of Electromagnetic Waves and Applications*, 25:13,1886-1894, DOI: 10.1163/156939311797453962

Yeow, Y. K. Abbas, Z.Khalid, K. (2010) Application of microwave moisture sensor for determination of oil palm fruit ripeness. *MeasSci Review* 10 (1): 7-14.