# Dielectric Behavior of Natural Rubber Composites in Microwave Fields

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**ABSTRACT:** In this article, we report the preparation of conducting natural rubber (NR) with polyaniline (Pani). NR was made into a conductive material by the compounding of NR with Pani in powder form. NR latex was made into a conductive material by the *in situ* polymerization of aniline in the presence of NR latex. Different compositions of Pani–NR semi-interpenetrating networks were prepared, and the dielectric properties of all of the samples were determined in microwave frequencies. The cavity perturbation technique was used for this study. A HP8510 vector network analyzer with a rectangular cavity resonator was used for this study. S bands 2–4 GHz in frequency were used. Thermal studies were also carried out with thermogravimetric analysis and differential scanning calorimetry. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2682–2686, 2007

**Key words:** composites; conducting polymers; conjugated polymers; dielectric properties

## INTRODUCTION

The incorporation of a conducting polymer into a host polymer substrate to form a blend, composite, or interpenetrated bulk network has been widely used as an approach to combine electrical conductivity with desirable physical properties of polymers.[1,2] Polyaniline (Pani) is considered one of the most promising candidates for the fabrication of conductive blends or composites within an industrially important class of polymers.[3]

Interpenetrating network conducting composites result from the *in situ* polymerization of monomers of conducting polymers inside the matrices of conventional linear polymers. This can be done by a chemical or electrochemical polymerization method. The electrochemical method uses[4,5] an electrode coated with conventional polymers. In chemical polymerization,[6–8] oxidizing agents such as ferric chloride or cupric chloride are incorporated into the polymer film. The film is then exposed to the monomer vapor or to a solution of the monomer in an appropriate liquid.

There are a number of articles dealing with conducting composites and blends. The direct-current and alternating-current conductivity of Pani–poly(vinyl alcohol) blends[9] and Pani–zinc sulfide composites were studied in microwave fields.[10] Banerjee and Mandal[11,12] prepared blends of HCl-doped Pani nanoparticles with poly(vinyl chloride) (PVC). Pani–

PVC composite films prepared by solution blending in the presence of phosphoric acid and HCl as the dopants have also been reported.[13,14] A processable Pani–PVC composite was prepared by the dispersion of Pani into a PVC matrix by mechanical mixing and compression molding in a hot press.[15] The electrochromic behavior of Pani–PVC composite films with structural changes in Pani with the use Fourier transform infrared studies were also reported.[16] Kaiser et al.[17] recently reported conductivity and thermopower data for Pani blends with PVC, which showed an increase in conductivity at lower temperatures.

As far as the processability and mechanical properties are concerned, the modification of conducting Pani at the microlevel needs to be accomplished. The incorporation of flexible elastomers into relatively rigid Pani's through blending,[18,19] *in situ* polymerization,[20] or interpenetrating networks[21,22] has attracted considerable attention. Copolymers with core–shell structures have also been chosen. On the basis of this concept, polybutadiene rubber latex covalently bonded with water-soluble Pani as the shell was reported.[23] Conductivity is also imparted by the addition of finely divided fillers of high intrinsic conductivity, such as carbon black.[24,25] Also, the plastics are made into conductive materials by solution blending,[26,27] dry blending, or melt processing.[28]

Among conductive elastomers, natural rubber (NR) has the potential for optoelectrical applications. With its easy processability, cost effectiveness, and mechanical properties, conducting NR holds a better position than all of the conductive elastomers. Very few articles have been published on the conductivity of NR.[29] We

attempted to make a conducting NR by the *in situ* polymerization of aniline in the presence of NR latex. The dielectric properties of the semi-interpenetrating networks (SIPNs) were determined.

## EXPERIMENTAL

### Materials

Our materials included ISNR-5, compounding ingredients, Pani, aniline, NR latex, Vulkastab VL, ammonium persulfate, and 1M HCl.

### Preparation of the Pani–NR SIPN

NR latex was first stabilized with Vulkastab VL and was converted to positively charged latex (positex) with HCl to avoid coagulation during polymerization. Also, the positive latex helped in the preparation of the doped Pani–NR SIPN. Aniline was added to positively charged latex and was then polymerized with ammonium persulfate as an initiator. The reaction was carried out at room temperature for 4 h. Different proportions of Pani–NR SIPNs, say, 2 : 1, 1 : 1, and 1 : 2, were prepared, and the dielectric properties were studied at microwave frequencies.

The *in situ* polymerization of aniline in the presence of positive NR latex caused it to lose its film properties. This phenomenon indicated that the Pani molecules bound the rubber particles. The Pani-bound NR latex was stable, and it could be considered a NR-modified water-soluble Pani latex. With the stability of Pani latex and also the difficulty for the formation of film, the nature of SIPN could be considered a core–shell structure, that is, a Pani shell with a NR core, as in Pani-coated polystyrene latex[30] and poly-butadiene–poly(styrene-co-styrene sulfonate) (PSS) latex. The positively charged NR latex and Pani were typically covalently bonded, as reported for the core shell structures of water-soluble Pani–polybutadiene latex.[23]

To take the measurements, the material was coagulated with NaOH solution. It was then doped with 1M HCl. After coagulation, we made a uniform sheet of the NR–Pani compound by passing it through the tight nip of a two-roll mill. After coagulation, the Pani–NR SIPN was found to be soluble in toluene and could be made into a film very easily.

### Application study: Antistatic chappel

An antistatic chappel was prepared with the 2 : 1 Pani–NR SIPN. The SIPN was prepared by the *in situ* polymerization of aniline in the presence of NR latex as explained earlier. The SIPN was coagulated, doped with 1M HCl, washed, and dried, and it was used to prepare the chappel. The chappel compound was pre-

### TABLE I
### Formulations

| Material | A1 | A2 | A3 | A4 |
|---|---|---|---|---|
| NR | 70 | 70 | 70 | 70 |
| HSR | 30 | 30 | 30 | 30 |
| ZnO | 5 | 5 | 5 | 5 |
| Stearic acid | 6 | 6 | 6 | 6 |
| Microcrumb | 40 | 40 | 40 | 40 |
| Clay | 60 | 60 | 60 | 60 |
| Silica | 10 | 10 | 10 | 10 |
| Paraffin oil | 4 | 4 | 4 | 4 |
| SP | 1 | 1 | 1 | 1 |
| Vulcafor F | 1.2 | 1.2 | 1.2 | 1.2 |
| S | 2.3 | 2.3 | 2.3 | 2.3 |
| DNPT | 6 | 6 | 6 | 6 |
| CBS | 1 | 1 | 1 | 1 |
| TMTD | .2 | .2 | .2 | .2 |
| Pani–NR SIPN | 0 | 2 | 4 | 6 |

HSR, high styrene rubber; SP, styrenated phenol; S, sulphur; DNPT, di nitroso pentamethylene tetramine; CBS, N-cyclohexyl-2-benzthiazyl sulphonamide; TMTD, tetramethyl thiuram disulphide.

pared with the formulation given in Table I. Four mixes were prepared, that is, A1 to A4, with varying parts per hundred resin of the 2 : 1 Pani–NR SIPN.

## SETUP AND THEORY

The dielectric properties of Pani and its composites were measured with the cavity perturbation technique.[31] The experimental setup[32] consisted of a HP8510 vector network analyzer, sweep oscillator, and rectangular cavity resonator (Rohde & Schwarz India Pvt., Ltd.). The measurements were done at 25°C in the S band (2–4 GHz). In the cavity perturbation technique for the accuracy of results, the volume of the sample ($V_s$) should be less than 1/1000th of the volume of the cavity ($V_c$). Because of this size limitation, the measurements on powder and pellet samples were conducted in the S band only. When a dielectric material was introduced in a cavity resonator at the position of maximum electric field, the contribution of magnetic field for the perturbation was minimum. The field perturbation was given by Kupfer et al.[33]:

$$-\frac{d\Omega}{\Omega} \approx \frac{(\bar{\varepsilon}_r - 1) \int\limits_{V_s} E \times E_0^* dV}{2 \int\limits_{V_c} |E_0|^2 dV} \quad (1)$$

where $d\Omega$ is the complex frequency shift; $E$ and $E_0$ are the perturbed and unperturbed fields in the cavity, respectively; and $\bar{\varepsilon}_r$ is the relative complex permittivity of the sample material. $d\Omega$ is related to the quality factor ($Q$) as

$$\frac{d\Omega}{\Omega} \approx \frac{d\omega}{\omega} + \frac{j}{2}\left[\frac{1}{Q_S} - \frac{1}{Q_0}\right] \quad (2)$$

$Q_s$ and $Q_0$ are the quality factors of the cavity with and without sample. $Q$ is given by

$$Q = f/\Delta f$$

where $f$ is the resonant frequency and $\Delta f$ is the corresponding 3-dB bandwidth. For small samples, we assumed that $E = E_0$ and for the dominant $TE_{10p}$ mode in a rectangular wave guide:

$$E_0 = E_{0\max} \sin(\pi x/a) \sin(\pi pz/d), p = 1, 2, 3 \ldots \quad (3)$$

From eqs. (1)–(3), the real part of the relative complex permittivity ($\varepsilon_r'$) and imaginary parts of the relative complex permittivity ($\varepsilon_r''$) are given by

$$\varepsilon_r' = 1 + \frac{f_o - f_s}{2f_s}\left(\frac{V_c}{V_s}\right)$$

$$\varepsilon_r'' = \frac{V_c}{4V_s}\left(\frac{Q_o - Q_s}{Q_oQ_s}\right)$$

where $\varepsilon_r'$ is generally known as the dielectric constant and $\varepsilon_r''$ is related to the dielectric loss of the material.

The loss tangent (tan δ) is given by

$$\tan\delta = \sigma + \omega\varepsilon''/\omega\varepsilon'$$

where $\sigma + \omega\varepsilon''$ and $\omega\varepsilon'$ is the effective conductivity of the medium. When σ due to free charge is negligibly small (good dielectric), the effective conductivity is due to electric polarization ($\sigma_e$) and is reduced to

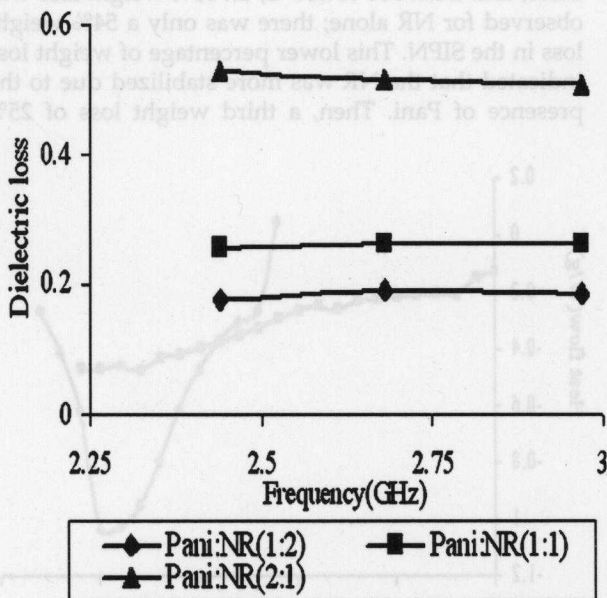$$\sigma_e = \omega\varepsilon'' = 2\pi f\varepsilon_0\varepsilon_r''$$



**Figure 1** Variation of dielectric loss with frequency for the Pani–NR composites.
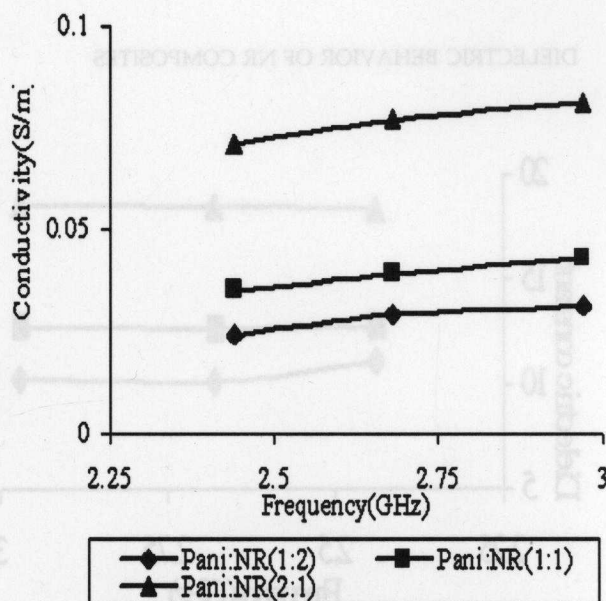
**Figure 2** Variation of conductivity with frequency for the Pani–NR composites.

The efficiency of heating is usually compared by means of a comparison coefficient ($J$), which is defined as[34]

$$J = 1/\varepsilon_r \tan\delta$$

The absorption of electromagnetic waves when it passes through the medium is given by the absorption coefficient ($\alpha_f$),[34] which is defined as

$$\alpha_f = \varepsilon_r'' f/nc$$

where $n = \sqrt{\varepsilon^*}$ and $c$ is the velocity of light.

Penetration depth, also called skin depth ($\delta_f$), is basically the effective distance of penetration of an electromagnetic wave into the material[35]:

$$\delta_f = 1/\alpha_f$$

## RESULTS AND DISCUSSION

### Dielectric properties of the conducting NR latex

Dielectric loss and conductivity

The effect of frequency on dielectric loss and conductivity was very small as shown in Figures 1 and 2. In the microwave field, a dielectric loss and conductivity occurred due to the dipolar polarization under the influence of an alternating-current field. The dielectric loss was constant with change in frequency. This may have been due to the firm contact of Pani molecules with the nonpolar NR through the core–shell structure. Because the conductivity was directly related to the dielectric loss, it also showed the same behavior
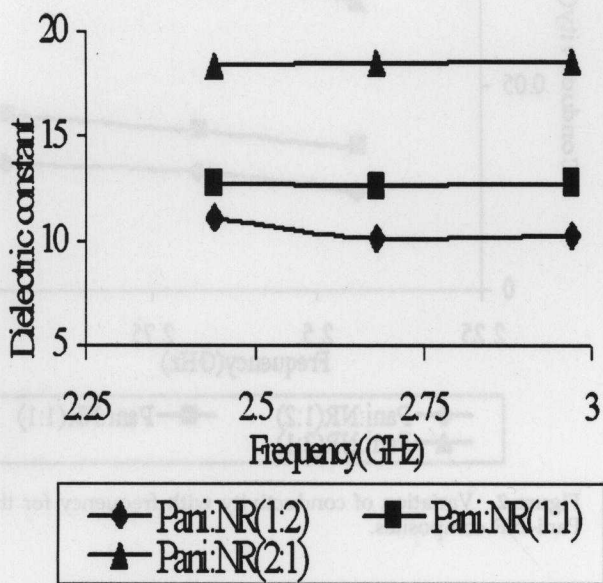
**Figure 3** Variation of dielectric constant with frequency for the Pani–NR composites.

as that of dielectric loss. It was also evident, as shown in the figures, that the dielectric loss and conductivity were higher for the 2 : 1 Pani–NR composition due to the higher percentage of Pani.

### Dielectric constant

Figure 3 shows the variation of the dielectric constant with frequency. It is clear from the figure that the dielectric constant was also less affected by the change in frequency. However, there was a shift of values in the dielectric constant from the normal dielectric constant of NR (i.e., 2) due to the presence of Pani. The dielectric constant was higher for the 2 : 1 composition.

### $\alpha_f$ and $\delta_f$

Table II shows $\alpha_f$ (absorption coefficient) and $\delta_f$ (penetration depth) for different proportions of Pani–NR in the SIPN. As shown in Table II, $\alpha_f$ was high and $\delta_f$ was low for the 2 : 1 composition. NR allowed the passage of electromagnetic radiation, and when the Pani content was increased, the electromagnetic radiations were restricted to penetration.

**TABLE II**
**Variation of $\alpha_f$ and $\delta_f$ of the Pani–NR Composites at 2.97 GHz**

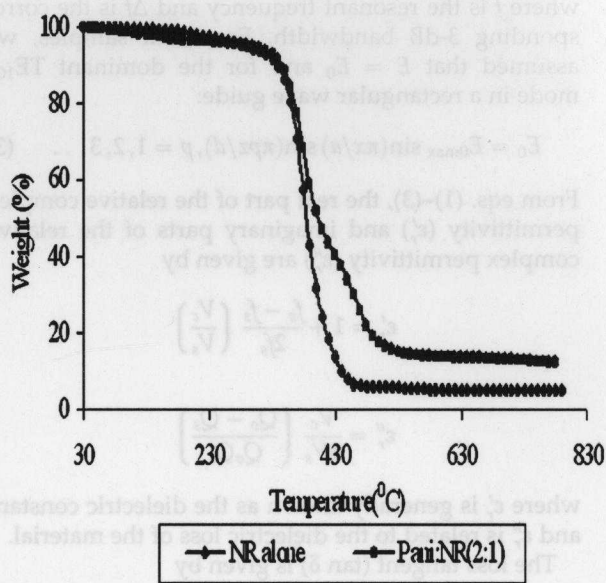| Property | Composition (Pani–NR) | | |
|---|---|---|---|
| | 2 : 1 | 1 : 1 | 1 : 2 |
| $\alpha_f$ (m$^{-1}$) | 3.5 | 2.27 | 1.73 |
| $\delta_f$ (m) | 0.28 | 0.44 | 0.58 |



**Figure 4** TGA thermogram of NR and the Pani–NR composites.

### Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies

Figure 4 shows the TGA of NR alone and that of the 2 : 1 Pani–NR SIPN. As shown clearly in the figure, there was a weight loss of 6% up to 300°C in both cases, and from 300 to 450°C, an 85% weight loss was observed for NR alone; there was only a 54% weight loss in the SIPN. This lower percentage of weight loss indicated that the NR was more stabilized due to the presence of Pani. Then, a third weight loss of 25%
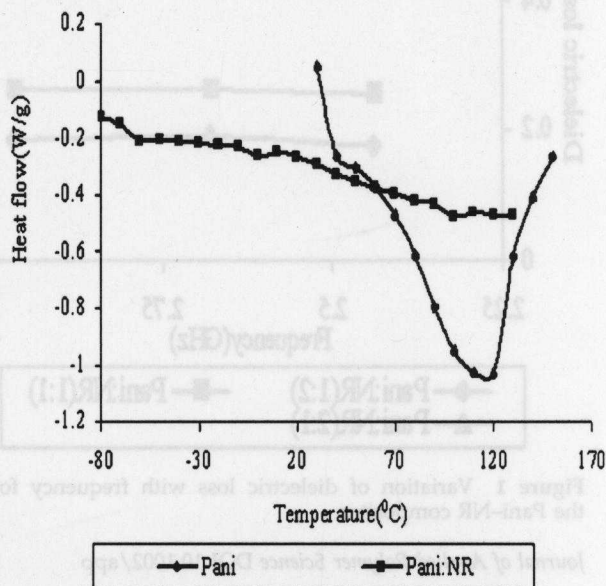


**Figure 5** DSC thermogram of NR and the Pani–NR composites.

**TABLE III**
**Dielectric Loss and Conductivity of the Chappel**

| 2 : 1 Pani (phr) | Dielectric loss | Conductivity (S/m) |
|---|---|---|
| 0 | 0.034 | $4 \times 10^{-5}$ |
| 2 | 0.163 | $2.03 \times 10^{-4}$ |
| 4 | 0.235 | $2.9 \times 10^{-4}$ |
| 6 | 0.257 | $3.2 \times 10^{-4}$ |

was observed at a temperature range of 450–550°C due to the degradation of Pani. When the core–shell structure was formed by the *in situ* polymerization of aniline in the presence of positively charged NR latex, the covalent bond formed increased the degradation temperature. That is, the SIPN had to break the covalent bond formed first, and then, the NR chain degraded. This may be the reason why the thermal stability of the SIPN increased.

Figure 5 shows the DSC thermogram of Pani and the Pani–NR SIPN. It is clear from the figure that the glass-transition temperature of NR shifted to −65°C and that of Pani shifted to 105°C. The lower glass-transition temperature shift of Pani was due to the presence of more flexible NR.

## Application study: Antistatic chappels

Table III shows the conductivity and dielectric loss of the antistatic chappels prepared. Clearly, the conductivity and dielectric loss of the compound were slightly increased, which indicated that the compound dissipated current as heat energy.

## CONCLUSIONS

NR was successfully made into a conductive material by the *in situ* polymerization technique. The 2 : 1 Pani–NR SIPN gave better dielectric properties. The dielectric constant was improved by the *in situ* technique. The thermal degradation stability of NR was increased due to the presence of Pani. The conducting NR could be used in various applications, including antistatic coatings, antistatic chappels, and anticorrosion applications.

## References

1. Andreatta; Heeger, A. J.; Smith, P. Polym Commun 1990, 31, 275.
2. Im, S. S.; Byun, S. W. J Appl Polym Sci 1994, 51, 1221.
3. Chan, H. S. O.; Hopok, H.; Khor, E.; Tan, M. M. Synth Met 1995, 31, 95.
4. De Paoli, M. A.; Waltman, R. J.; Diaz, A. F.; Bargon, J. J Chem Soc Chem Commun 1984, 1015.
5. Han, J. H.; Matobe, T.; Whang, Y. E.; Miyata, S. Synth Met 1991, 45, 261.
6. Tieke, B.; Gabriel, W. Polymer 1990, 31, 20.
7. Makhlouki, M.; Morsli, M.; Bonnet, A.; Conan, A.; Pron, A.; Lefrant, S. J Appl Polym Sci 1992, 44, 443.
8. Mandal, T. K.; Mandal, B. M. Synth Met 1996, 80, 83.
9. Dutta, P.; Biswas, S.; Ghosh, M.; De, S. K.; Chatterjee, S. Synth Met 2001, 122, 455.
10. Pant, H. C.; Patra, M. K.; Vashistha, P.; Manzoor, K.; Vardera, S. R.; Kumar, N. Presented at the 14th Annual General Meeting and Theme Symposium on Novel Polymeric Materials, Mumbai, India, 2003.
11. Banerjee, P.; Mandal, B. M. Macromolecules 1995, 28, 3940.
12. Subramaniam, C. K.; Kaiser, A. B.; Gilberd, P. W.; Wessling, B. J Polym Sci Part B: Polym Phys 1993, 31, 1425.
13. Pron, A.; Osterholm, J. E.; Smith, P.; Heeger, A. J.; Laska, J.; Zagorska, M. Synth Met 1993, 57, 3520.
14. Thangarathinavelu, M.; Tripathi, A. K.; Goel, T. C.; Varma, I. K. J Appl Polym Sci 1994, 51, 1347.
15. Shacklette, L. W.; Han, C. C.; Luly, M. H. Synth Met 1993, 57, 3532.
16. Terlemezyan, L.; Mihailov, M.; Ivanova, B. Polym Bull 1992, 29, 283.
17. Kaiser, A. B.; Subramaniam, C. K.; Gilberd, P. W.; Wessling, B. Synth Met 1995, 69, 197.
18. Mantovani, G. L.; MacDiarmid, A. G.; Mattoso, L. H. C. Synth Met 1997, 84, 73.
19. Vallim, M. R.; Felisberti, M. I.; De Paoli, M. A. J Appl Polym Sci 2000, 75, 677.
20. Stejskal, J.; Sapurina, I.; Prokes, J.; Zemek, J. Synth Met 1999, 105, 195.
21. Wang, L. Y.; Chiang, L. Y.; Kuo, C. S.; Lin, J. G.; Huang, C. Y. Mater Res Soc Symp Proc 1996, 413, 571.
22. Chiang, L. Y.; Wang, L. Y.; Kuo, C. S.; Lin, J. G.; Huang, C. Y. Synth Met 1997, 84, 721.
23. Changshu, K.; Chiang, Y.; Jayant, K.; Tripathy, K. Polymer 2000, 41, 1768.
24. Medalia, A. I. Rubber Chem Technol 1986, 59, 432.
25. Poleey, M. H.; Boonstra, B. B. Rubber Chem Technol 1957, 30, 170.
26. Angelopoulos, M.; Patel, N.; Saraf, R. Synth Met 1993, 55, 1552.
27. Thangarathinavelu, M.; Tripathi, A. K.; Goel, T. C.; Varma, I. K. J Appl Polym Sci 1994, 51, 1347.
28. Shacklette, L. W.; Han, C. C.; Luly, M. H. Synth Met 1993, 57, 3532.
29. Sreeja, R.; Pradeep, P.; Rosamma, A. Kerala Sci Cong Proc 2003, 15, 631.
30. Barthet, C.; Armes, S. P.; Lascelles, S. F.; Luk, S. Y.; Stanley, H. M. E. Langmuir 1998, 14, 2032.
31. Mathew, K. T.; Raveendranath, U. In Sensors Update; Baltes, H.; Gopel, W.; Hesse, J., Eds.; Wiley-VCH: United Kingdom, 1998.
32. Mathew, K. T.; Raveendranath, U. Microwave Opt Technol Lett (USA) 1993, 6, 104.
33. Kupfer, K.; Kraszewski, A.; Knoochel, R. In Sensors Update; Wiley-VCH: Weinheim, 2000; Vol. 7, p 186.
34. Ku, C. C.; Liepins, R. Electrical Properties of Polymers: Chemical Principles; Hanser: Munich, 1987.
35. Bradford, L. S.; Carpentier, M. H. The Microwave Engineering Hand Book; Chapman & Hall: London, 1993.