

Effect of Drying Conditions on Microwave Conductivity of Polyaniline

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ABSTRACT: Polyaniline was synthesized by using ammonium persulfate initiator in the presence of 1M HCl. It was dried under different drying conditions like room temperature drying (for 48 h), oven drying (at 50–60°C for 8 h under a vacuum), and vacuum drying (at room temperature for 16 h). The conductivities of these samples were measured at microwave frequencies. These samples were also pelletized and the measurements were repeated. The cavity perturbation technique was used for the study. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2008–2012, 2002

Key words: polyaniline; conductivity; frequency

INTRODUCTION

Conducting polymers have been proved to be excellent replacements for metals and semiconductors in electrochemical applications, notably for the energy storage process, corrosion protection, electrochromic devices, electrochemical sensors, and so forth and above all as a strong electromagnetic imaging material.^{1,2} These uses have recently attracted significant attention from all branches of polymer research with a growing interdisciplinary trend. Electrically conducting polymers differ from inorganic crystalline semiconductors in two ways: they are molecular in character and lack long-range orders. With a large variety of conducting polymers, polyaniline (PAN) is a relatively stable, electrically conducting polymer resulting from the oxidative polymerization of aniline, which is easy to prepare. Also, the environmental stability of PAN appears to be

extremely good compared to a number of other conducting polymers. For this reason it is one of the most potentially useful conducting polymers.

Recently, La Croix and Diaz³ proposed that the thermal decomposition of the material occurs in two stages, although the thermal stability of PAN has been reported up to 400°C. Two studies^{4,5} subsequently reported a three-step decomposition process for the HCl protonated conducting form: the initial loss is due to volatilization of water molecules, the second loss is related to loss of dopant moiety, and the third loss is related to degradation of the polymer backbone due to production of gases such as acetylene and ammonia. The present article reports the effect of drying conditions on microwave conductivity of PAN at various frequencies.

EXPERIMENTAL

Materials

Reagent grade aniline was distilled prior to use. The HCl and ammonium persulfate were used as received.

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Table I Results of Pure Polyaniline Powder

Frequency (GHz)	Room Temp. Drying (48 h)	Oven Drying (8 h at 50–60°C)	Vacuum Drying (16 h at 28°C)
2.6S	Real = 12.3128	Real = 8.7712	Real = 12.7267
	Imag = 9.8054	Imag = 1.9812	Imag = 6.6646
	Cond = 1.4628	Cond = 0.2955	Cond = 0.9939
3.2S	Real = 11.5464	Real = 9.2441	Real = 9.6073
	Imag = 9.1273	Imag = 2.4281	Imag = 6.5399
	Cond = 1.6671	Cond = 0.4435	Cond = 1.1942
3.62	Real = 13.8470	Real = 8.3815	Real = 8.4765
	Imag = 8.9477	Imag = 2.2015	Imag = 7.9897
	Cond = 1.8013	Cond = 0.4435	Cond = 1.6090

Real, real part of complex permittivity; Imag, imaginary part of complex permittivity; and Cond, conductivity of the sample (S/m).

Table II Results of Pure Polyaniline Pellets

Frequency (GHz)	Room Temp. Drying (48 h)	Oven Drying (8 h at 50–60°C Under Vacuum)	Vacuum Drying (16 h at 28°C)
2.86	Real = 10.3276	Real = 7.0903	Real = 10.1776
	Imag = 0.4517	Imag = 0.1707	Imag = 0.9401
	Cond = 0.0719	Cond = 0.0272	Cond = 0.1496
3.9	Real = 11.8709	Real = 6.9380	Real = 10.0244
	Imag = 1.7346	Imag = 0.8693	Imag = 0.7891
	Cond = 0.3757	Cond = 0.1888	Cond = 0.1712

Preparation of PAN

Chemical oxidative polymerization of aniline was carried out using ammonium persulfate as an initiator in the presence of 1M HCl. The polymer formed was dried under different conditions like room temperature (for 48 h), under a vacuum (under a 1 kg/cm² vacuum for 16 h), and in a vacuum oven (at 50–60°C for 8 h). The dielectric properties and the conductivities of these samples were measured using the cavity perturbation technique.

The experimental setup consists of a HP8510 vector network analyzer, a sweep oscillator, a S-parameter test set, and a rectangular cavity resonator. The resonant frequency and quality (*Q*) factor of the cavity resonator with and without the samples in the cavity were measured and the dielectric parameters were evaluated. All the measurements were done in S band (2–4 GHz) at 25°C. The PAN samples were pelletized and the microwave conductivity of these samples was also measured using the same technique. In the mi-

crowave studies the conductivity (σ) is expressed in terms of the loss or imaginary part of the complex permittivity:

$$\sigma = 2 \prod f \epsilon_0 \epsilon''$$

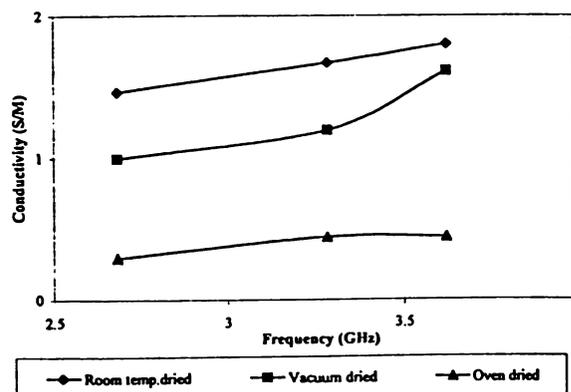


Figure 1 Variation of conductivity of PAN powder with frequency at different drying conditions.

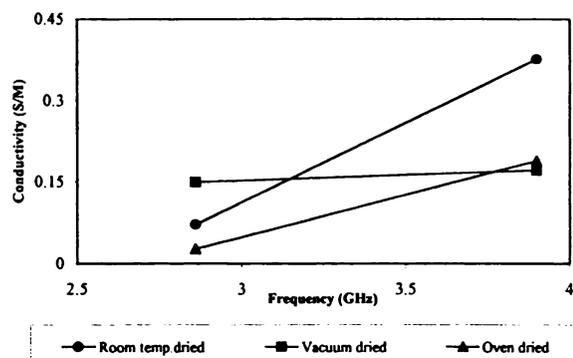


Figure 2 Variation of conductivity of PA pellet with frequency at different drying conditions.

where ϵ_0 is the permittivity of free space or a vacuum, ϵ_r'' is the imaginary part of the complex permittivity, and

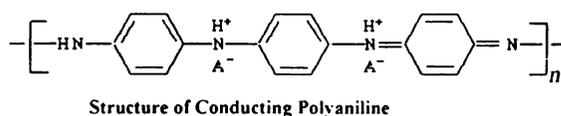
$$\epsilon_r'' = V_c/4V_s(1/Q_s - 1/Q_t)$$

where V_c is the volume of the cavity, V_s is the volume of the sample, Q_s is the quality factor of the cavity loaded with the sample, and Q_t is the quality factor of the cavity with the empty sample holder.

RESULTS AND DISCUSSION

Tables I and II show the conductivity values for PAN powder and pellet samples, respectively, under different drying conditions. The dielectric loss in all cases is found to increase with an increase in frequency.

Protonation in PAN leads to the formation of a radical cation by an internal redox reaction, which causes reorganization of the electronic structure to give semiquinone radical cations. The degree of protonation and the electronic conductivity thus become a function of the dopant concentration.



At low frequencies the dipoles synchronized their orientation with the field. However, as the frequency increases, the inertia of the molecule and the binding forces become dominant and it is the basis for dielectric heating or dielectric loss. Figures 1 and 2 show that the conductivity increases with the frequency in all cases, and it may

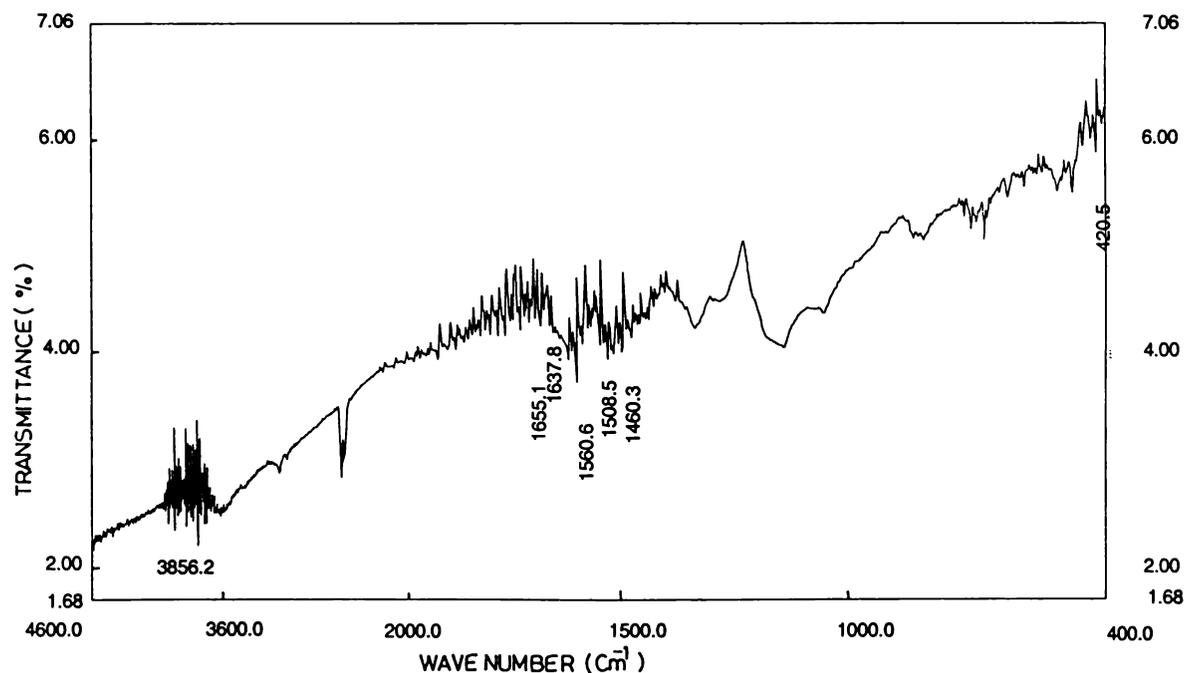


Figure 3 IR spectrum of room temperature dried PAN powder.

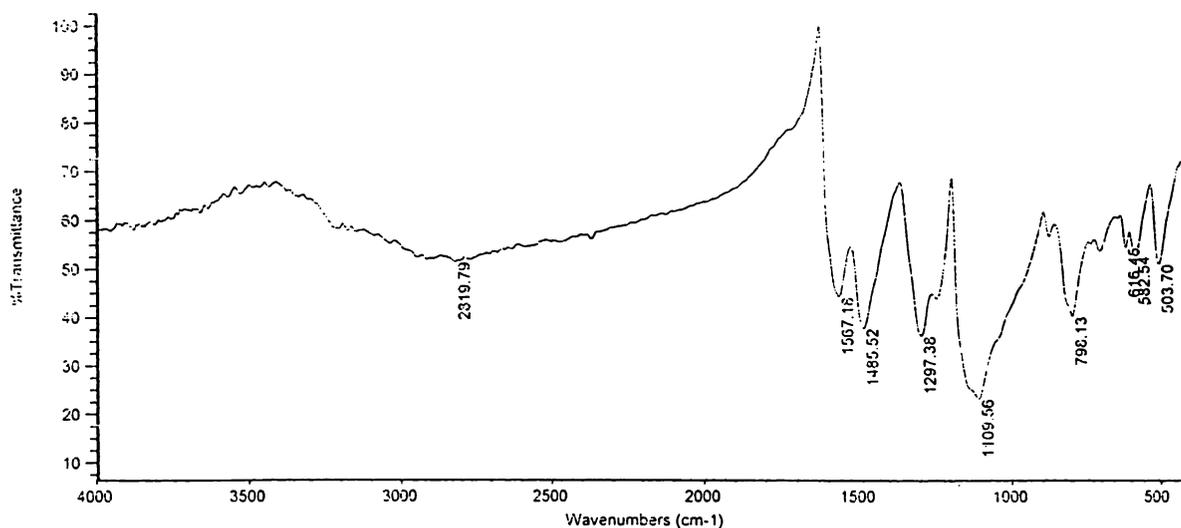


Figure 4 IR spectrum of vacuum dried PAN powder.

be due to the increase in the dielectric loss with the increase in frequency.

Tables I and II also show that the microwave conductivity of the room temperature dried powder form of PAN is greater compared to a vacuum dried sample, which is superior to the oven dried sample. Similarly, when the powder sample is converted to a pellet by applying pressure, the conductivity is reduced, irrespective of the drying conditions.

It is evident from the experiment that there is a loss of dopant molecules under a vacuum and

during high temperature drying, which will reduce the dielectric loss, which in turn reduces the conductivity. This is confirmed by the IR spectra of the various samples. Figures 3–5 show the IR spectra of powder samples that were room temperature dried, vacuum dried, and oven dried, respectively. In the IR spectra of the room temperature dried sample the principal absorption at 1150 cm^{-1} indicates the presence of PAN-HCl.⁶ The absorptions at 1325, 1275, 1150, and 1050 cm^{-1} shift to 1297, 1250, 1109.56, and 890 cm^{-1} , respectively, in the vacuum dried sample. It is

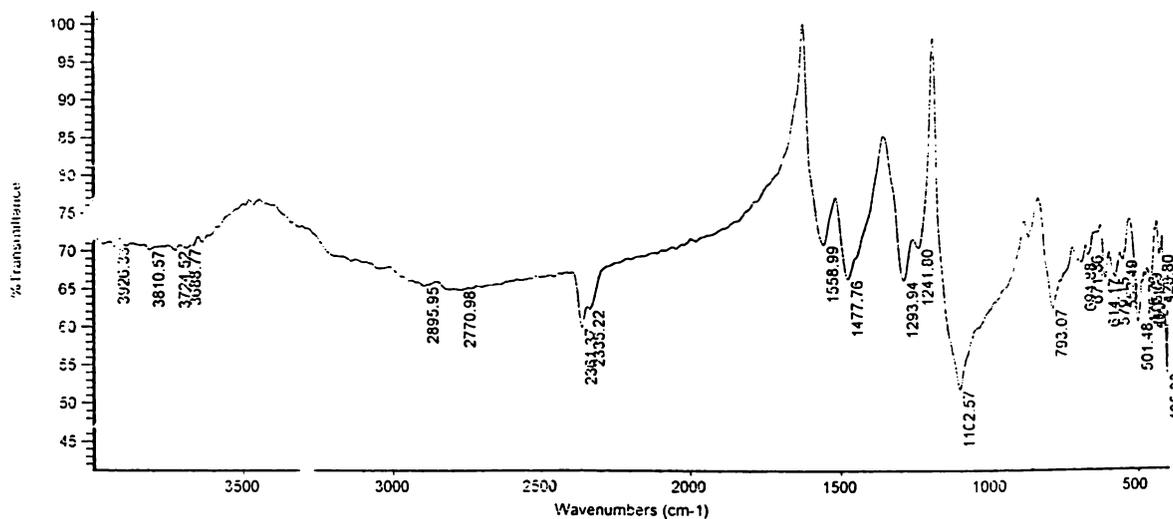


Figure 5 IR spectrum of oven dried PAN powder.

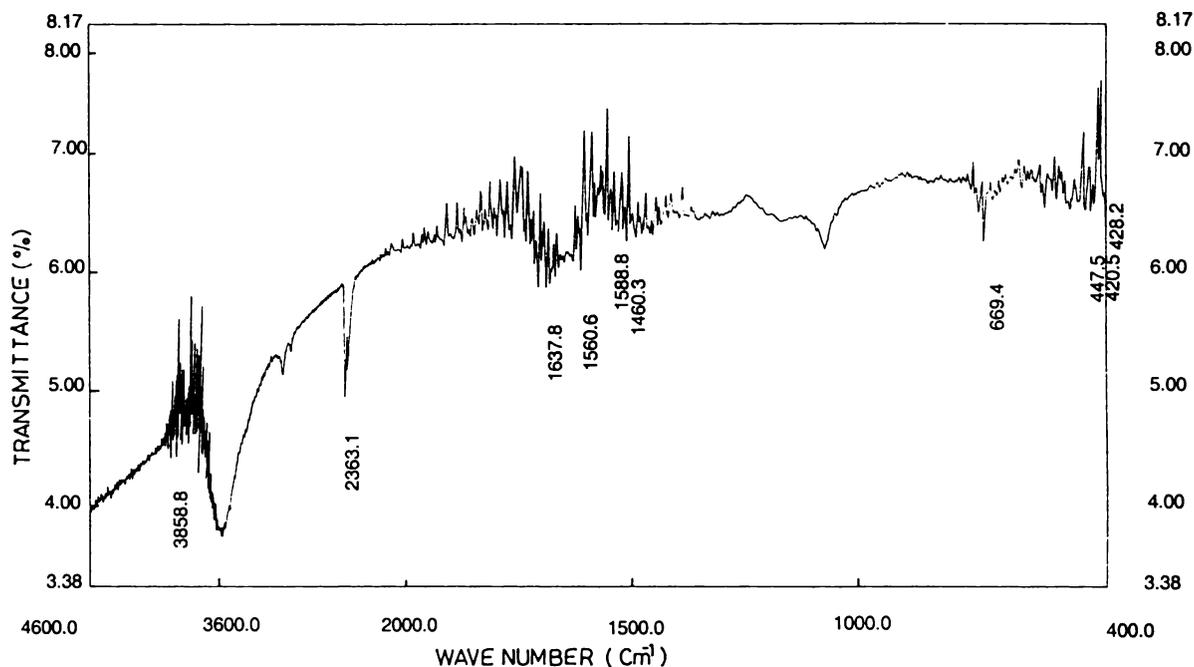


Figure 6 IR spectrum of room temperature dried PAN pellet.

shifted to 1293.94, 1241.8, 1102.57, and 862 cm^{-1} , respectively, in the oven dried sample. The low frequency shifts can be attributed to the deprotonation of the PAN salt.⁷

The same reason applies to the reduced conductivity of the pellet samples. The pellets are made by applying pressure, which may cause the loss of dopant molecules. Figure 6 shows the IR spectra of the room temperature dried pellet sample. In the IR spectra of the pellet sample the absorption peaks are shifted to 1315, 1160, 1075, and 1025 cm^{-1} , respectively, from that of the powder sample.

CONCLUSION

The microwave conductivity of PAN is found to be related to the dopant concentration. The conductivity is decreased when the amount of dopant molecules is decreased. The conductivity is found

to increase with the increase in frequency. The drying condition is found to affect the dopant concentration in PAN.

REFERENCES

1. Lee, N. Li; Ong, L. H. *J Appl Electrochem* 1992, 22, 512.
2. Trinidal, M. F.; Montemayer, C.; Falas, E. *J Electrochem Soc* 1991, 138, 3186.
3. La Croix, J. C.; Diaz, A. F. *J Electrochem Soc* 1988, 135, 1457.
4. Patil, S. F.; Bedaker, A. G.; Agastic, C. *Mater Lett* 1992, 14, 307.
5. Chan, H. S. O.; Hopok, H.; Khor, E.; Tan, M. M. *Synth Met* 1995, 31, 95.
6. Saravanan, V.; Palaniappan, S.; Seetharamu, S. *Macromol New Frontiers* 1995, 1, 344.
7. Anand, J.; Swapna Rao, P.; Palaniappan, S.; Sathyanarayana, D. N. *Macromol New Frontiers* 1998, 1, 374.