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Der Pharma Chemica, 2013, 5(1):320-326
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Study of temperature effect on binary mixtures of polyamide with phenol derivatives using TDR

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ABSTRACT

Dielectric measurements of nylon-6 & nylon-11 with substituted phenols p-cresol, m-cresol and o-cresol mixture in different concentrations over the frequency range from 10 MHz- 20 GHz was carried out using the Time Domain Reflectometry (TDR). By least square fit method, the dielectric parameters such as static dielectric constant (ε_0), dielectric constant at high frequency (ε_∞) and relaxation time (τ) were extracted from complex permittivity spectra at temperature range from 40^0C to 15^0C. Here we are discussing the temperature effect on these binary mixtures.

Keywords: Nylon-6 & nylon-11, Dielectric parameters; Time Domain Reflectometry (TDR)

INTRODUCTION

The polyamides are the most successful class of plastic materials in the market. The main applications of polyamides are in fibers, film, and injection-molded engineering plastics. Polyamides are crystallizing out fast and exhibiting good mechanical strength and chemical resistance [1]. During recent years, several attempts to modify polyamides to improve mechanical performance or achieve new desirable properties have been published in the literature [2]. The mixing of polyamide with phenol is as an alternative route to achieve new property combinations, especially for attaining high thermal stability [3-5].

Dielectric method is an important tool to understand the weak molecular interactions. Many researchers have explored to understand intra and inter molecular hydrogen bonding and molecular dynamics of binary and tertiary mixtures in polar and non-polar solvents [6].

Temperature influence on dielectric properties depends on intermolecular hydrogen bond of amide and phenol groups, which have been discussed in relations with the molecular behaviour.

Here, we report the temperature influenced dielectric parameter of binary mixtures of nylon-6 and nylon-11 with the substituted phenols such as p-cresol, m-cresol and o-cresol in the frequency range of 10MHz to 20GHz using Time Domain Reflectometry.

MATERIALS AND METHODS

(1) Chemicals and sample preparation:
Sigma-Aldrich variety of nylon-6 & nylon-11and E-merk variety of *p*-Cresol, *m*-Cresol and *o*-Cresol samples were used without further purification. Nylon-6 & nylon-11 (w/v) was varied from 0.2 0.6 and 1 % added to 50, 60, 70, 80, 90 and 100% (v/v) of phenol derivatives. The solution were prepared and kept at room temperature. The mixture was undisturbed for 3 days to achieve complete solubility and analyzed in TDR.

(2) TDR setup and data acquisition:
The complex permittivity spectra were studied using Time Domain Reflectometry [7-9]. The Hewlett-Packard HP 86100C sampling oscilloscope with HP 54754A TDR plug-in module was used. A fast rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance 50Ω. Transmission line system under test was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell with 3.5mm outer diameter and 1.35mm effective pin length. All measurements were done under open load conditions, the thermostat has been used to maintain the constant temperature in sample cell within the accuracy limit of ± 1^{o}C. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, a time window of 5 ns was used. The reflected pulses without sample $R_0(t)$ and with sample $R_x(t)$ were digitized in 1024 points in the memory of the oscilloscope.

(4) Data Analysis:
The time dependent data were processed to obtain complex reflection coefficient spectra ρ*(ω) over the frequency range from 10MHz to 20MHz using Fourier transformation as [10-12],

$$\rho^*(\omega) = \frac{C}{j\omega d}\frac{p(\omega)}{q(\omega)} \text{ ---------- (1)}$$

where ρ(ω) and q(ω) are Fourier transforms of [$R_0(t)-Rx(t)$]) and [$R_0(t)+Rx(t)$] respectively, c is the velocity of light, ω is angular frequency, d is the effective pin length and $j = \sqrt{-1}$ .The complex permittivity spectra ε*(ω) were obtained from reflection coefficient spectra ρ*(ω) by applying the bilinear calibration method [7]. Fig.1 shows the complex permittivity dispersion spectrum for 0.8 wt % nylon-6 with *o*-Cresol.

The experimental values of ε* are fitted with the Debye equation [13] with ε_0, ε_∞, and τ as fitting parameters. A nonlinear least squares fit method [14] was used to determine the values of dielectric parameters. In equation (2), ε_0 is the static dielectric constant, ε_∞ is the limiting high-frequency dielectric constant and τ is the relaxation time.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1+(j\omega\tau)\ ]} \text{ ------(2)}$$

RESULTS AND DISCUSSION

The results of ε_0 and τ for binary mixtures were obtained by fitting experimental data with the Debye equation, and listed in Tables [1-2]. The concentration of polyamide increased at low temperature when the dielectric constant was high and vice versa. The increase in static permittivity [Fig 2-4] with decrease in temperature could be due to the increase in peptide molecules which led to increase in the orientation and interfacial polarization [15]. The relaxation time [Fig 5-7] was decreased with the increase of temperature, which may be due to inverse relation of orientation polarization and temperature. The relaxation time decreases as the chain length increases, but this assumption may not be applicable for the principal relaxation of high polymers. In such cases, the relaxation is associated not with rotation of the molecule as a whole, but rather with segmental motion in the chain. Therefore, we have observed decrease in relaxation time [16]. There was a major change observed in dielectric constant values when increasing wt% of substituted phenols than increase of polyamide wt%.

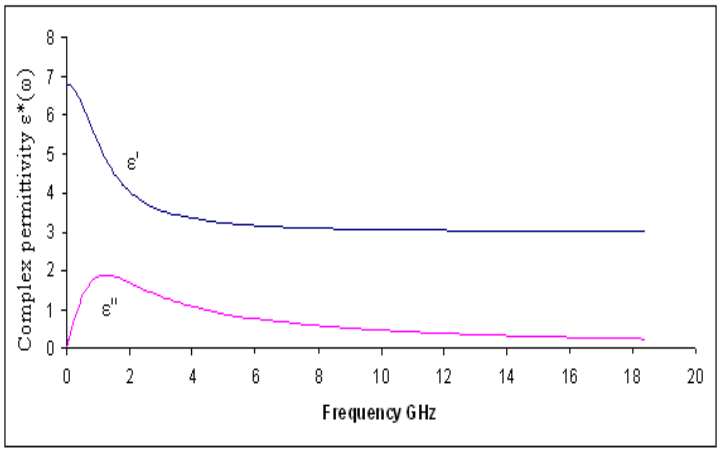

Figure 1 Complex permittivity dispersion spectrum for 0.8 wt % Nylon-6 with *o*-Cresol

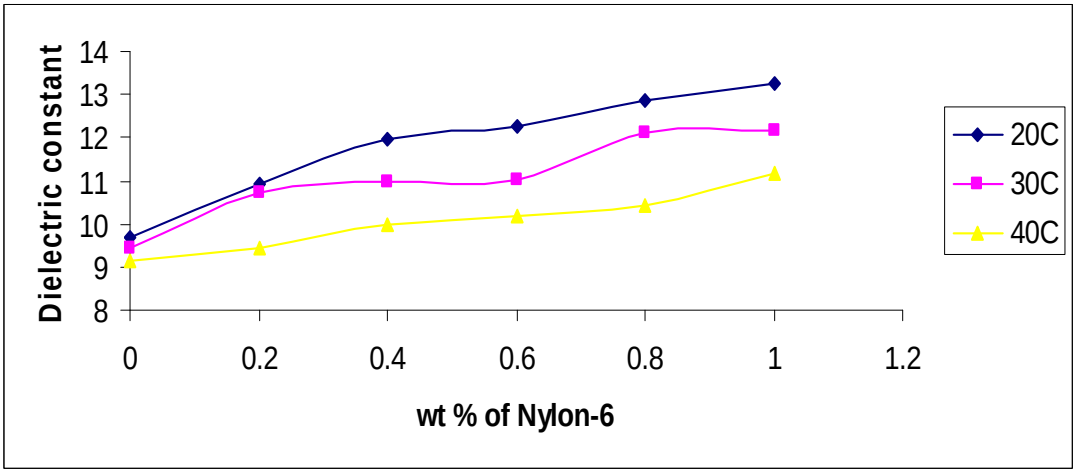

Figure 2 Dielectric constant of Nylon-6 with *p*-Cresol at different temperature

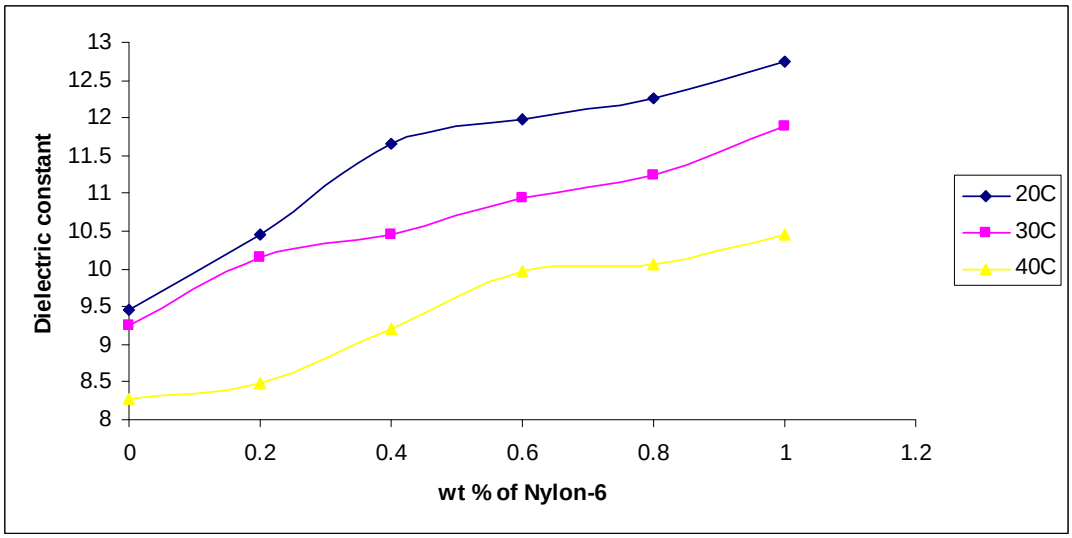

Figure 3 Dielectric constant of Nylon-6 with *m*-Cresol at different temperature

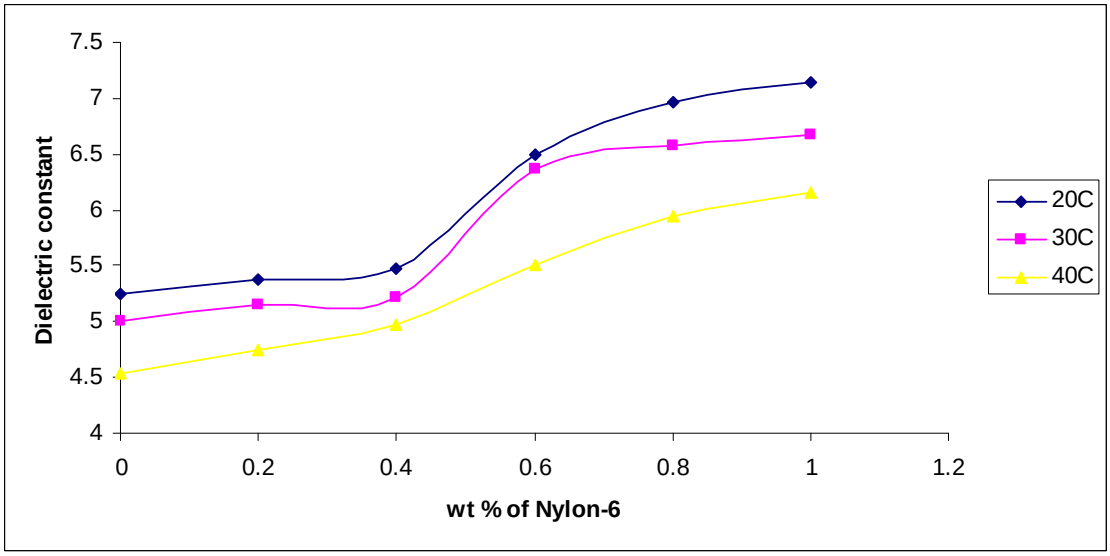

Figure 4 Dielectric constant of Nylon-6 with *o*-Cresol at different temperature

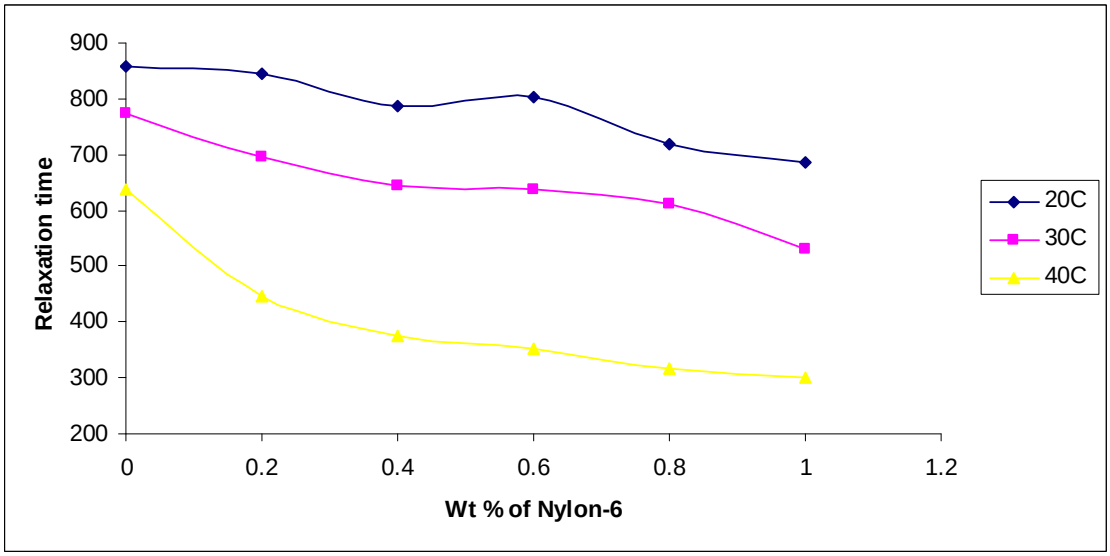

Figure 5 Relaxation time of Nylon-6 with *p*-Cresol at different temperature

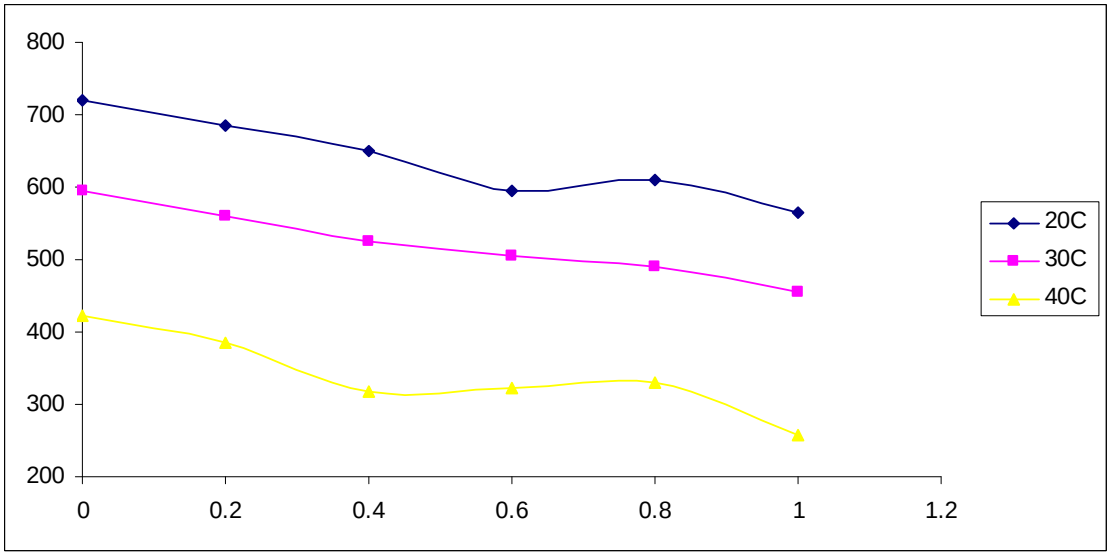

Figure 6 Relaxation time of Nylon-6 with *m*-Cresol at different temperature

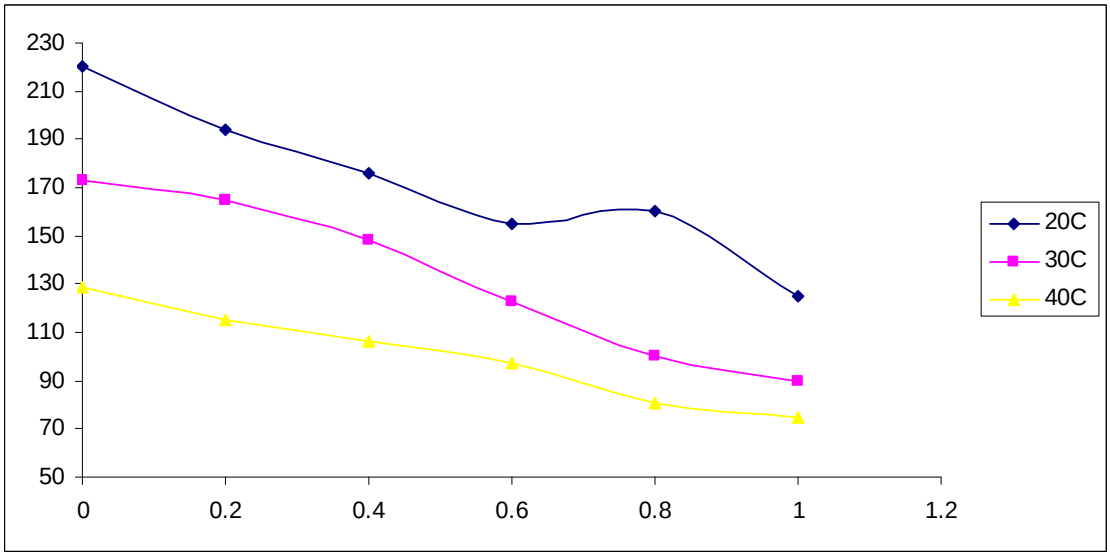

Figure 7 Relaxation time of Nylon-6 with *o*-Cresol at different temperature

Table 1: Static dielectric constant and relaxation time for nylon-6-with binary mixtures at different temperatures

Wt % of Nylon-6+	20^0C		30^0C		40^0C	
	ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)
p-Cresol						
0	9.70	858	9.43	773	9.15	637
0.2	10.91	846	10.73	697	9.45	445
0.4	11.95	788	10.96	645	10.00	375
0.6	12.25	803	11.03	637	10.20	351
0.8	12.87	719	12.11	611	10.45	318
1.0	13.25	685	12.15	532	11.15	300
m-Cresol						
0	9.45	720	9.26	596	8.27	422
0.2	10.45	684	10.15	559	8.48	385
0.4	11.65	650	10.45	524	9.20	318
0.6	11.98	595	10.95	505	9.97	322
0.8	12.25	610	11.25	491	10.06	330
1.0	12.75	565	11.90	455	10.45	258
o-Cresol						
0	5.25	220	5.00	173	4.53	129
0.2	5.37	194	5.15	165	4.75	115
0.4	5.48	176	5.22	148	4.97	106
0.6	6.50	155	6.37	123	5.50	110
0.8	6.97	160	6.58	100	5.95	91
1.0	7.15	125	6.67	90	6.15	80

Table 2: Static dielectric constant and relaxation time for nylon-11-with binary mixtures at different temperatures

Wt % of Nylon-11+	20^0C		30^0C		40^0C	
	ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)
p-Cresol						
0	9.70	858	9.43	773	9.15	637
0.2	11.45	754	11.31	668	10.22	578
0.4	12.25	677	12.10	524	10.45	450
0.6	12.50	625	12.19	514	11.45	400
0.8	13.35	580	12.25	466	12.05	365
1.0	13.51	525	12.35	463	12.30	333
m-Cresol						
0	9.45	720	9.26	596	8.27	422
0.2	10.75	664	10.44	509	9.28	393
0.4	11.85	630	11.26	494	9.40	344
0.6	12.18	565	11.39	445	10.47	329
0.8	12.75	510	11.53	441	10.56	302
1.0	13.15	485	11.62	435	10.85	238
o-Cresol						
0	5.25	220	5.09	165	4.53	129
0.2	5.57	184	5.53	153	4.96	99
0.4	5.78	155	5.57	128	5.24	87
0.6	6.75	129	6.60	103	5.71	83
0.8	7.15	118	6.65	95	6.15	79
1.0	7.36	102	6.70	80	6.33	75

CONCLUSION

We have carried out the dielectric properties at high frequency range for nylon-6 & nylon 11 with phenol derivative mixtures. Temperature effect on nylon-6 & nylon 11 strongly influences the dielectric parameters. The dielectric constant was high and relaxation time was low for nylon 11 compared to nylon-6.

Acknowledgements
The authors express their sincere thanks to Prof. S. C. Mehrotra, Department of Computer Science and Information Technology, Dr. B. A. M. University, Aurangabad, India for his guidance to evaluate the dielectric parameters. The financial assistance from DRDO and DST, New Delhi, India is greatly acknowledged.

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