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Study of fluid structure of polyamide-6 with polar/apolar solvents using dielectric parameters

P. Mohan Kumar [1], **M. Malathi** *[2]

[1]*Department of Physics, K.S.S.E.M, Bangalore, Karnataka, India*
[2]*Condensed Matter Research Lab, VIT University, Vellore, Tamil Nadu, India*

ABSTRACT

Fluid mixture of polyamide-6 (PA6) with phenol derivatives and in apolar solvents were prepared at different concentrations, the dielectric relaxation measurements were measured in the frequency range of 10 MHz- 20 GHz at 303K using the Time Domain Reflectometry. The dielectric parameters such as static dielectric constant (ε_0), relaxation time (τ) were found and discussed to yield information on the molecular structure and dynamics of the mixture. The dielectric constant and relaxation time for binary and tertiary mixture were found to be high in the order of PA6 with p-Cresol>m-Cresol>o-Cresol and in CCl_4>benzene>1, 4-dioxane.

Keywords: Polyamide (PA 6); Dielectric constant; Relaxation time; Dielectric spectroscopy.

INTRODUCTION

Polyamides consist of methylene segments $(CH_2)_n$ separated by amide units (-CO-NH-) and are packed either parallel or antiparallel in their structure. Polyamides usually exhibit high modulus, toughness and strength, low creep and wide applications including fibers and engineering thermoplastics [1]. Polyamide-6 (PA 6) is widely used in manufacturing of gears, fittings, bearings, electrical switches, bobbins, and connectors, power tool housings, wheelchair wheels and automotive cooling fans etc., [2]. Polyamides with variable chain lengths form a family of engineering resins. The dynamics of polyamides have been extensively studied with the help of mechanical and dielectric techniques [3-5]. Recently, polymer dielectric measurements have become popular to monitor polymer material fabrication.

Dielectric studies involve the measurement of permittivity and dielectric loss. The measurements can be used to find dielectric constant and relaxation time. The relaxation time depends upon the molecular size, shape, intramolecular and intermolecular forces, and can be used to investigate molecular and intramolecular motions and their relation to molecular structures [6]. The intra and intermolecular hydrogen bonding has a considerable effect on the microscopic as well as macroscopic properties and plays a vital role in understanding the dielectric behavior of polymers [7]. The H-bond between two neighboring polymeric groups can be altered with the addition of polar solvents [8-10].

Mixture of polyamides and phenols serves as a humidity sensing materials. There is no appropriate report on the dielectric studies of polyamides with phenol derivatives. Hence in this work, authors made an attempt to study the effect of polyamide/ solvent interactions and its molecular association of PA 6 with phenol derivatives and in apolar solvents over the frequency range of 10MHz to 20GHz at 303K using Time Domain Refractrometry (TDR).

MATERIALS AND METHODS

(1) *Chemicals and sample preparation*

Binary sample preparation: Sigma-Aldrich variety of PA 6 and E-merk variety of *p*-Cresol, *m*-Cresol and *o*-Cresol samples were used without further purification. PA6 (w/v) was varied from 0.2 to 1.0 % and added to *p*-Cresol, *m*-Cresol and *o*-Cresol. The solutions were prepared and kept at room temperature. The mixture was undisturbed for three days to achieve complete solubility and analyzed in TDR.

Tertiary sample preparation:

0.2, 0.6 and 1 % of binary mixture were diluted with the CCl_4, benzene and 1, 4-dioxane and analyzed in TDR.

(2) *TDR setup and data acquisition*:

The complex permittivity spectra were studied using Time Domain Reflectometry [11-13]. 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^oC. 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.

(3) *Data Analysis*:

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10MHz to 20MHz using Fourier transformation as [14-16],

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

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 [11]. Fig.1 shows the complex permittivity dispersion spectra of 0.2 wt% PA 6 with p-Cresol.

The experimental values of ε* are fitted with the Debye equation [17]

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

with ε_0, ε_∞, and τ as fitting parameters. A nonlinear least squares fit method [18] 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.

RESULTS AND DISCUSSION

From our binary results the dielectric constant of PA6 increases and the relaxation time decreases with increasing concentrations of substituted phenols (Figs.2-3). The dielectric constant increased due to the intermolecular interaction between PA 6 and phenol derivatives. The relaxation time increases 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 [19].

The dielectric constant of *o*-Cresol–PA6 mixture, the values are quite low compared to *m*-Cresol and *p*-Cresol. Due to the presence of methyl group in ortho position, the intra molecular H- bond interaction of *o*-Cresol is high. In addition steric effect also occurs within *o*-Cresol. The combined effects led to decrease in the molecular interaction between PA6 and *o*-Cresol (Fig.5). Hence it has been shown that the PA 6 with *o*-Cresol mixture was giving low dielectric constant and relaxation time.

In the case of PA6- *m*-Cresol mixture, the dielectric parameter exhibited lower value than *p*-Cresol mixture (Fig.6). In *p*-Cresol, methyl groups are away from H-bonding region and also self association may occur which led to high dielectric constant of PA6 with *p*-Cresol mixture (Fig.4).

The static dielectric constant (ε_0) and relaxation time (τ) for tertiary mixtures were obtained by fitting experimental data with the Debye equation, were listed in Tables [1-3]. The results indicate when the concentrations of PA6 and substituted phenols increase the relaxation time and dielectric constant are also increased. The polyamide with substituted phenols mixture was highly diluted by non-polar solvents, which may reduce the H-bonding interaction of the complexes, hence the dielectric constant and relaxation time was very low in lower wt %. There was a major change observed in dielectric constant values when increasing wt% of substituted phenols than increase in PA6 wt%.

From our results, polyamide with substituted phenols mixture in CCl_4 was showing the high dielectric constant and relaxation time. In the presence of CCl_4, the phenol may be self associated there by forming H-bonded multimers. Due to the self association of phenols, the molecular interaction between polyamide and phenol mixture is enhanced, which leads to increase in the dielectric constant and relaxation time in CCl_4 (Fig.7).

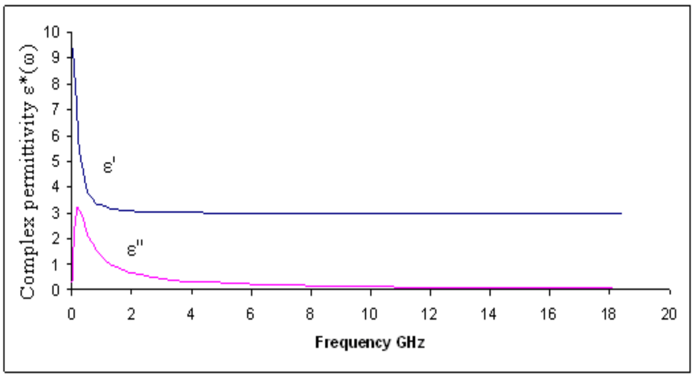


Figure 1 Complex permittivity dispersion spectrum for 0.2 wt % PA-6 with *p*-Cresol.

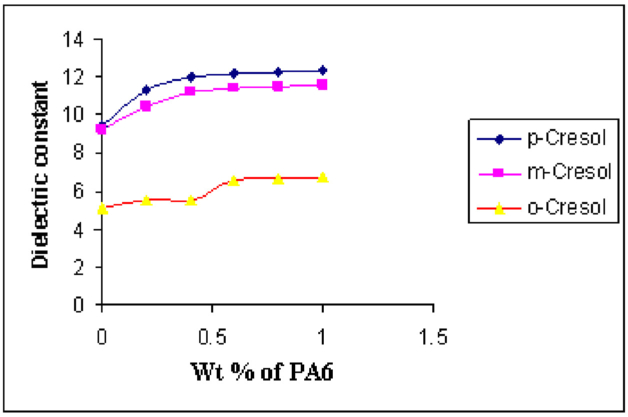


Figure 2 Wt % of PA6 vs dielectric constant

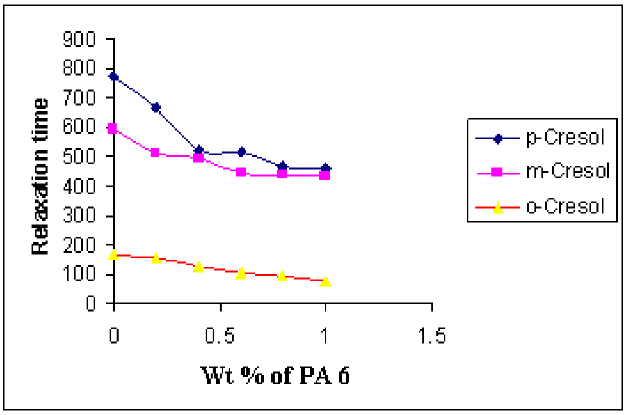


Figure 3 Wt % of PA 6 vs relaxation time

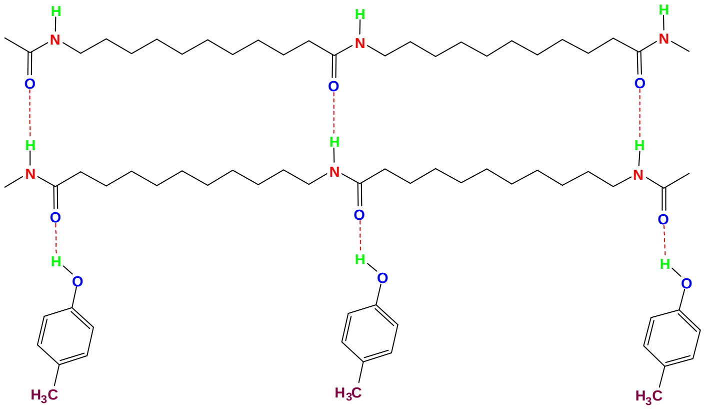


Figure 4 Schematic representation of interaction of PA 6 with *p*-Cresol

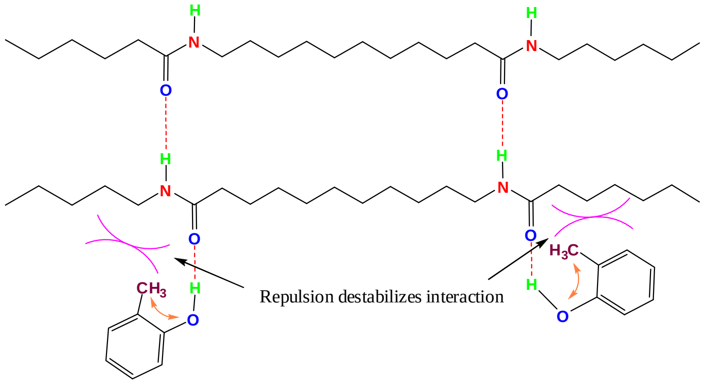


Figure 5 Schematic representation of interaction of PA 6 with *o*-Cresol

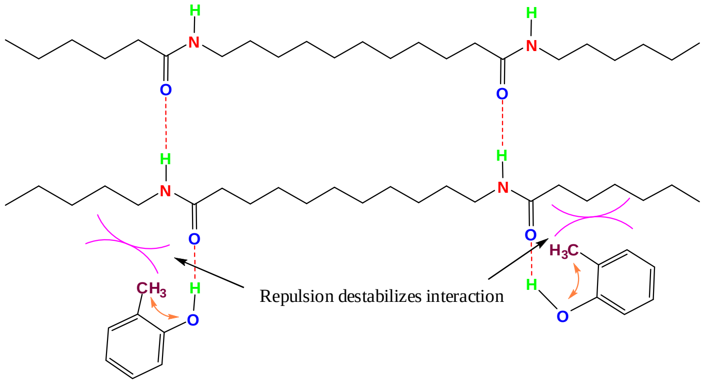
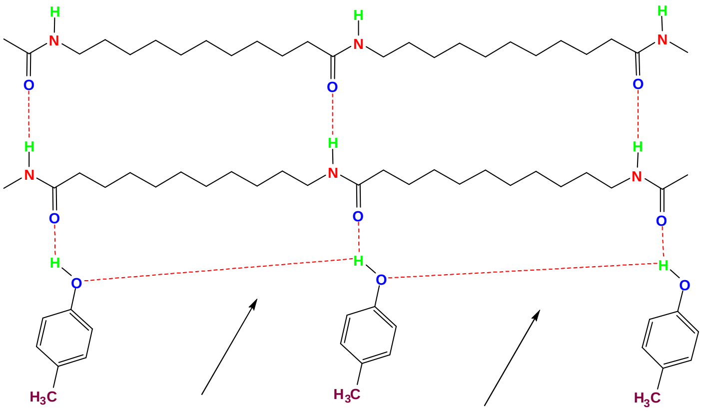


Figure 6 Schematic representation of interaction of PA 6 with *m*-Cresol

In the case of benzene both monomer and multimer are formed, but in the presence of 1, 4-dioxane monomerization must be completed in phenols. Hence the relaxation time and dielectric constant was very low in 1, 4- dioxane. The results were in good agreement with our previous work [20] and also matched with sengwa et al. [21] who discussed the role of non-polar solvents in polymers.

Table 1 Variation of dielectric parameters for PA6 with *p*-Cresol in non-polar solvents at 303K.

Wt % of PA6	Wt% of *p*-Cresol	CCl_4		Benzene		1, 4-dioxane	
		ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)
0.2%	50%	5.37	200	5.15	155	5.04	93
	60%	6.62	232	6.25	200	5.77	110
	70%	8.13	268	7.35	235	6.80	129
	80%	9.64	266	8.45	305	8.00	173
	90%	10.23	279	10.05	362	9.87	259
	100%	10.73	697	10.73	697	10.73	697
0.6%	50%	5.40	215	5.35	195	3.96	-
	60%	6.75	240	6.45	215	5.03	101
	70%	8.20	252	8.00	242	5.93	158
	80%	9.70	275	9.15	300	7.14	245
	90%	10.55	295	10.35	294	8.79	328
	100%	11.03	637	11.03	637	11.03	637
1%	50%	5.59	221	5.47	215	-	-
	60%	6.95	240	6.64	222	5.92	104
	70%	8.85	269	8.14	245	6.93	133
	80%	9.96	281	9.35	275	8.06	181
	90%	10.78	372	10.54	346	9.95	275
	100%	12.11	532	12.11	532	12.11	532



CCl_4 enhances intermolecular H-bonding between *p*-Cresol;
1, 4-dioxane not favouring intermolecular H-bonding

Figure 7 Schematic representation of polymer-phenol interaction in tertiary mixture.

Table 2 Variation of dielectric parameters for PA6 with *m*-Cresol in non-polar solvents at 303K.

Wt % of PA6	Wt% of *m*-Cresol	CCl_4		Benzene		1, 4-dioxane	
		ε_0	τ (ps)	ε_0	τ (ps)	ε_0	τ (ps)
0.2%	50%	4.75	246	4.70	192	4.60	102
	60%	6.27	252	6.10	225	5.35	132
	70%	7.71	267	6.95	257	6.01	149
	80%	8.88	289	7.25	280	7.30	203
	90%	10.09	307	8.95	295	8.66	264
	100%	11.80	444	11.80	444	11.80	444
0.6%	50%	4.95	252	4.90	200	4.85	122
	60%	6.56	286	6.25	216	5.40	145
	70%	7.77	315	7.44	277	6.55	164
	80%	9.15	339	9.15	295	7.35	231
	90%	10.25	385	9.45	305	8.75	338
	100%	11.85	364	11.85	364	11.85	364
1%	50%	5.16	284	-	-	-	-
	60%	6.50	290	6.46	215	5.48	159
	70%	7.67	295	7.55	245	6.75	175
	80%	8.93	327	8.85	300	7.44	217
	90%	10.18	338	9.95	325	9.00	295
	100%	12.00	353	12.00	353	12.00	353

Table 3 Variation of dielectric parameters for PA6 with *o*-Cresol in non-polar solvents at 303K.

Wt % of PA6	Wt% of *o*-Cresol	CCl_4		Benzene		1, 4-dioxane	
		ε_0	τ(ps)	ε_0	τ (ps)	ε_0	τ (ps)
0.2%	50%	3.90	150	2.45	124	2.15	85
	60%	4.18	136	3.95	115	3.55	-
	70%	4.21	125	4.05	99	3.95	75
	80%	5.77	114	4.55	88	4.55	70
	90%	6.42	87	5.00	80	4.95	80
	100%	7.41	84	7.41	84	7.41	84
0.6%	50%	4.00	125	3.00	115	2.25	80
	60%	4.25	110	3.55	100	4.18	74
	70%	4.32	104	4.00	94	4.63	75
	80%	5.95	95	4.67	85	5.28	70
	90%	6.64	90	5.23	80	5.73	77
	100%	7.55	82	7.55	82	7.55	82
1%	50%	4.15	106	3.55	105	3.00	82
	60%	4.67	94	4.25	96	4.00	72
	70%	5.36	83	4.67	88	4.25	75
	80%	6.15	82	4.95	75	5.15	85
	90%	6.73	81	5.75	70	5.85	95
	100%	7.63	82	7.63	82	7.63	82

CONCLUSION

We have carried out the dielectric properties at high frequency range for polyamide-phenol mixtures. Based on the results observed in our work, we have noticed mixing of polyamide-phenol derivatives at appropriate level strongly influences the dielectric parameters. Because, the polarity of polyamide enhanced during the interaction with phenol leads to the mixture suitable for humidity studies. Moreover, the dimensional changes occurring of the polyamide during the interaction with phenol strongly affect the moisture absorption property. Hence, it is quite helpful while manufacturing such polymer based humidity devices

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