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Der Pharma Chemica, 2012, 4 (2):800-807
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Solvent effect dielectric relaxation studies of polystyrene using TDR

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ABSTRACT

Using the Time Domain Reflectometry (TDR), dielectric relaxation studies were carried out on polystyrene-with substituted phenols *p*-cresol, *m*-cresol and *o*-cresol mixture in different non-polar solvents CCl_4 , benzene and 1, 4-dioxane for various concentrations over the frequency range from 10 MHz- 20 GHz at 303K. The dielectric parameters such as static dielectric constant (ϵ_0), relaxation time (τ) were found and discussed to yield information on the molecular interaction of the system. The dielectric constant and relaxation time were increased with the increase of wt % of polystyrene were noticed. The FTIR analysis was supporting the dielectric results. The intermolecular interaction has been discussed using the excess parameters like excess permittivity (ϵ^E) and excess inverse relaxation time ($1/\tau$)^E.

Keywords: Polystyrene (PS); Dielectric parameters; Excess parameters; Time Domain Reflectometry (TDR).

INTRODUCTION

Polystyrene is the fourth largest volume commodity thermoplastic, ranking behind polyethylene, polypropylene, and poly (vinyl chloride). Therefore, polystyrene, being a transparent, stiff material with high electrical resistance and low dielectric loss, is one of the most used commodity polymers in the application for packing, filtration, plastic models, CD and DVD cases, smoke detector housings, etc. PS possesses a very low dielectric loss (ϵ'') and very high resistivity [1].

The dielectric properties of polymers and polymer blends depend in general on the structure, crystallinity, morphology, and presence of other additives. In heterogeneous polymer blends, the permittivities of the polymers are influenced by interfacial effect (i.e., due to the polarization arising from the differences in conductivities of the two phases) [2].

Researchers have attempted to derive information about intra and inter molecular hydrogen bonding and molecular dynamics in binary mixtures and tertiary mixtures in polar and non-polar solvents for molecular conformations [3]. Shinyashiki et al [4-5] have extensively investigated the broadband dielectric study of dynamics of polymer and solvent in poly (vinyl pyrrolidone)/ normal alcohol mixtures and poly (vinyl pyrrolidone) –Ethylene glycol oligomer blends at various concentrations using TDR. The electrical properties of nanostructured sequential interpenetrating polymer networks and its morphology of natural rubber and polystyrene were studied using transmission electron microscopy and scanning electron microscopy [6]

In this present work, measurement of dielectric parameters and excess values of polystyrene-phenol mixtures with non-polar solvents at room temperature in the frequency range 10MHz to 20GHz were performed using Time Domain Reflectometry (TDR) to clarify the solvent effect on polystyrene. The samples were also characterized by FTIR to support the dielectric results.

MATERIALS AND METHODS

(1) Chemicals and sample preparation:

Sigma-Aldrich variety of polystyrene and E-merk variety of *p*-Cresol, *m*-Cresol and *o*-Cresol samples were used without further purification. PS (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 mixture was undisturbed for 4 days to achieve complete solubility and further diluted with non-polar solvents and analyzed in FTIR and TDR.

(2) FT-IR analysis:

The FTIR spectrum of polystyrene-phenol derivatives fluid mixtures was taken in a liquid sample cell and recorded FTIR spectrums using Nicolat Avator 330 spectrometer at 303K.

(3) 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°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 $\rho^*(\omega)$ 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 $\rho(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_0(t)-R_x(t)]$ and $[R_0(t)+R_x(t)]$ 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 $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying the bilinear calibration method [7]. Fig.1 shows the complex permittivity dispersion spectrum for 0.2 wt % polystyrene with *p*-Cresol in 1, 4-dioxane

The experimental values of ϵ^* are fitted with the Debye equation [13]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau)]} \text{-----} (2)$$

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.

RESULTS AND DISCUSSION

The FT-IR spectrum of transmittance in OH region (3200-3600cm⁻¹) for solvent mixtures and polymer solution was reported by Musa Kaleem Baloch and Mohsan Nawaz [15]. FT-IR spectrum of neat polystyrene showed

characteristic absorption peaks between 2900-3100 cm^{-1} for aromatic C-H/C-CH₂ reported by Yeonhwa Wi et al and Hong-wen wang et al [16-17]. We have recorded the FTIR spectrum in the region of 3800-2800 cm^{-1} as shown in Figs.2, noticed that there was an appreciable change in absorbance for the polystyrene with phenol derivatives in non polar solvents. In the presence of CCl₄ absorption is more compare to benzene and 1, 4-dioxane.

The results ϵ_0 and τ for tertiary mixtures were obtained by fitting experimental data with the Debye equation, were listed in Tables [1-3]. It is clear that when the concentration of PS increases the dielectric constant and relaxation time was increased. This increase in static permittivity is due to the increase in styrene molecules which leads to an increase in the orientation polarization and to the presence of interfacial polarization [1,18], and 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]. There was a major change observed in dielectric constant values when increasing wt% of substituted phenols than increase in PS wt%.

From our results, PS with substituted phenols mixture in CCl₄ was showing the high dielectric constant and relaxation time. In the presence of CCl₄, the phenol may be self associated there by forming H-bonded multimers. Due to the self association of phenols, the molecular interaction between polystyrene and phenol mixture is enhanced, which leads to increase in the dielectric constant and relaxation time in CCl₄ (Table 1).

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.

Excess Parameters

There is no appropriate molecular theory available in the literature which correlated dielectric relaxation parameters to solute-solvent interaction [22]. The excess parameters related to ϵ_0 and τ provides valuable information regarding interaction between the solute-solvent (polar-polar) liquid mixtures. These properties are also useful for detection of the cooperative domain in the mixture due to intermolecular interaction. Many authors reported the excess permittivity and inverse relaxation time for alcohols, amides, amines etc. [23-25].

According to literature survey, for the first time we have calculated the Excess permittivity and Inverse relaxation time for polystyrene-phenol fluid mixtures.

The information related to polystyrene and substituted phenols interaction may be obtained by excess permittivity (ϵ^E) and excess inverse relaxation time $(1/\tau)^E$ [25]. The excess permittivity can be defined as

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_1 X_1 + (\epsilon_0 - \epsilon_\infty)_2 X_2] \quad (3)$$

where X is mole fraction, w is weight in gm, m is molecular weight. The subscripts 1, 2 and m represent cresol, polystyrene and mixture respectively.

The excess permittivity may provide qualitative information about solute-solvent interaction in the mixture as follows:

- 1] $\epsilon^E = 0$: indicates the polystyrene and cresol do not interact at all.
- 2] $\epsilon^E < 0$: indicates the polystyrene and cresol interaction in such a way that the total effective dipoles get reduced.
- 3] $\epsilon^E > 0$: indicates the polystyrene and cresol interaction in such a way that the total effective dipole moment increases and dipoles aligned in parallel direction.

Similarly, the excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_1 X_1 + (1/\tau)_2 X_2] \quad (4)$$

where $(1/\tau)^E$ is the excess inverse relaxation time. The information regarding the dynamics of polystyrene and cresol interaction from this excess property is as follows:

- 1] $(1/\tau)^E = 0$: There is no change in the dynamics of polystyrene and cresol interaction.
- 2] $(1/\tau)^E < 0$: The polystyrene and cresol interaction produces a field such that the effective dipoles rotate slowly.
- 3] $(1/\tau)^E > 0$: The polystyrene and cresol interaction produces a field such that the effective dipoles rotate rapidly. i.e. the field will co-operate in rotation of dipoles.

The variation of excess permittivity ϵ^E and inverse relaxation time $(1/\tau)^E$ with mole fraction of polystyrene were shown in Figs. 3-4.

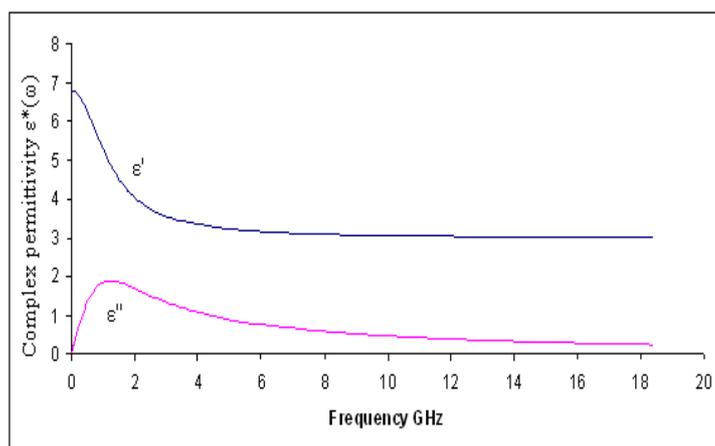


Figure 1 Complex permittivity dispersion spectrum for 0.2 wt % polystyrene with *p*-Cresol in 1, 4-dioxane

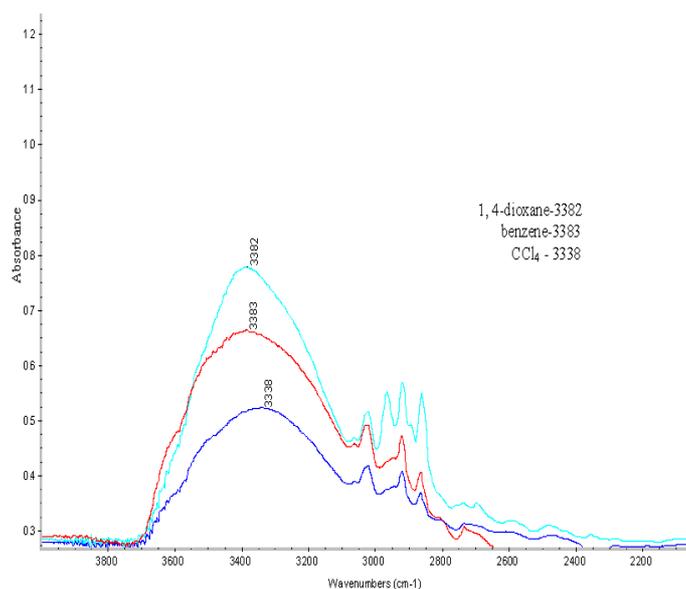


Figure 2 FT-IR spectrum of 0.2 wt % polystyrene+ *p*-Cresol+ (1, 4-dioxane, benzene, CCl₄)

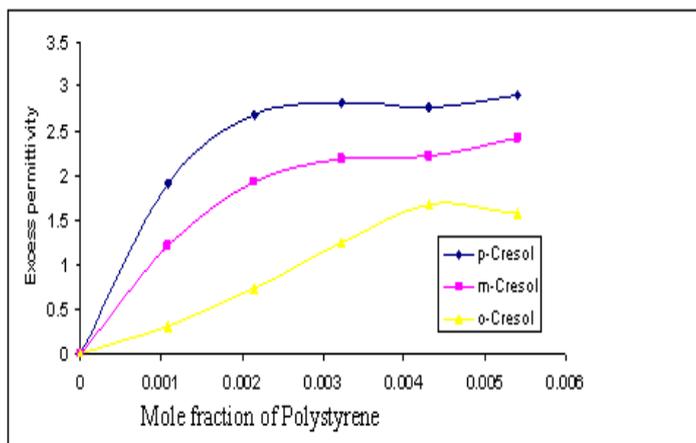


Figure 3 Mole fraction of polystyrene vs excess permittivity

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

Wt % of Polystyrene	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%	5.48	380	5.35	119	5.26	76
	60%	6.67	422	6.30	133	5.86	84
	70%	7.29	429	7.03	158	6.94	103
	80%	8.40	442	8.36	209	8.24	150
	90%	10.75	481	10.65	250	9.79	198
	100%	11.37	529	11.37	529	11.37	529
0.6%	50%	5.58	269	5.52	129	5.43	79
	60%	6.74	270	6.24	139	6.06	87
	70%	7.86	288	7.99	179	7.02	113
	80%	8.71	302	9.42	242	8.42	175
	90%	11.40	441	10.95	273	9.91	200
	100%	11.80	480	11.80	480	11.80	480
1%	50%	5.97	217	5.75	135	5.62	82
	60%	7.20	229	6.45	145	6.25	94
	70%	8.45	251	8.27	185	7.85	124
	80%	9.71	317	9.67	306	9.00	195
	90%	11.83	322	11.25	327	10.04	206
	100%	12.03	411	12.03	411	12.03	411

Table2: Variation of dielectric parameters for polystyrene with *m*-Cresol in non-polar solvents at 303K.

Wt % of Polystyrene	Wt% of <i>m</i> -Cresol	CCl ₄		Benzene		1, 4-dioxane	
		ϵ_0	τ (ps)	ϵ_0	τ (ps)	ϵ_0	τ (ps)
0.2%	50%	-	-	3.51	95	5.15	94
	60%	6.16	285	5.99	158	5.73	113
	70%	7.44	290	8.15	162	6.54	133
	80%	8.65	338	8.98	207	7.91	181
	90%	10.04	389	10.41	256	9.30	238
	100%	11.61	395	11.61	395	11.61	395
0.6%	50%	4.50	215	4.50	110	5.20	96
	60%	6.25	289	6.15	165	5.83	115
	70%	7.65	300	7.45	185	6.60	140
	80%	8.90	340	9.20	210	8.00	185
	90%	10.56	390	10.86	279	9.50	255
	100%	11.88	410	11.88	410	11.88	410
1%	50%	4.72	229	5.74	120	5.25	98
	60%	6.45	295	6.39	180	5.69	119
	70%	7.89	309	7.63	208	6.68	148
	80%	8.75	345	9.28	239	7.81	195
	90%	10.95	395	10.03	291	9.40	270
	100%	12.02	450	12.02	450	12.02	450

Table3: Variation of dielectric parameters for polystyrene with *o*-Cresol in non-polar solvents at 303K.

Wt % of Polystyrene	Wt% of <i>o</i> -Cresol	CCl ₄		Benzene		1, 4- dioxane	
		ϵ_0	τ (ps)	ϵ_0	τ (ps)	ϵ_0	τ (ps)
0.2%	50%	2.45	65	-	-	-	-
	60%	4.20	72	3.35	70	3.00	65
	70%	4.82	75	4.45	73	4.25	70
	80%	5.82	79	5.75	75	5.60	73
	90%	6.53	80	6.25	78	6.03	75
	100%	7.50	89	7.50	89	7.50	89
0.6%	50%	3.00	70	-	-	-	-
	60%	4.40	77	4.00	75	3.45	70
	70%	5.04	80	4.65	77	4.50	72
	80%	6.42	90	5.55	78	5.65	75
	90%	7.12	95	6.00	80	6.25	78
	100%	7.63	100	7.63	100	7.63	100
1%	50%	3.54	75	-	-	-	-
	60%	4.70	80	4.55	74	3.65	72
	70%	5.15	85	4.75	75	4.57	75
	80%	6.95	95	5.67	80	5.75	78
	90%	7.35	100	6.55	85	6.35	80
	100%	7.75	115	7.75	115	7.75	115

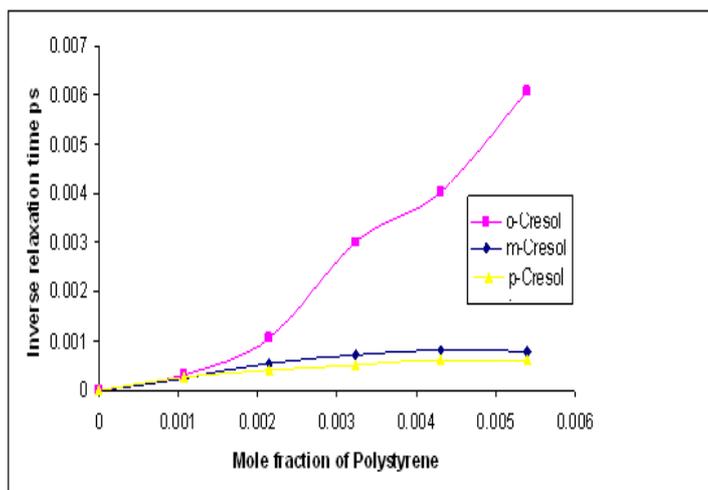


Figure 4 Mole fraction of polystyrene vs inverse relaxation time

CONCLUSION

We have carried out the dielectric properties at high frequency range for polystyrene-phenol derivative mixtures. Solvent effect on polystyrene strongly influences the dielectric parameters. The FTIR results, excess permittivity and excess inverse relaxation time indicate that intermolecular interaction which may be interpreted as complex formation between two interacting species via H-bonding between polystyrene and phenol derivatives.

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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