Journal of Polymer and Biopolymer Physics Chemistry, 2014, Vol. 2, No. 4, 73-77
Available online at http://pubs.sciepub.com/jpbpc/2/4/3

DOI:10.12691/jpbpc-2-4-3

Acoustical Investigations of Molecular Interactions in Polymer Solution of Pan/Clay Nano Composites and Dmso

D. P. Singh[1,*], Arun Upmanyu[2]

[1]Acoustics Research Centre, 4-215, Mississauga Valley Blvd., Mississauga, L5A 1Y7, ON, Canada
[2]Department of Physics, Rayat Bahra Institute of Engg. & Nano Technology, Hoshiarpur-146001, Punjab, India
*Corresponding author: drdpsn@hotmail.com

Received October 28, 2014; Revised November 17, 2014; Accepted November 26, 2014

Abstract Acoustical studies of intermolecular interactions in the polymer solution of PAN / clay nanocomposites and DMSO have been done at 30 degree Celsius using experimental ultrasonic velocity and density data taken from literature. Several acoustical and thermo-dynamical parameters such as isothermal compressibility, adiabatic compressibility, specific heat ratio, volume expansivity, surface tension, specific sound velocity, specific adiabatic compressibility, intermolecular free length, pseudo-Gruneisen parameter and classical absorption coefficient have been evaluated. Some elastic parameters such as Young modulus, shear modulus, bulk modulus and Poisson ratio have also been determined. Non linear parameters such as Moelwyn-Hughes parameter, reduced volume, reduced compressibility, Sharma's constants, Huggins parameter, isobaric acoustical parameter, isochoric acoustical parameter, isothermal acoustical parameter, fractional free volume, repulsive exponent, thermo acoustical parameter such as A*and B*, Bayer's non-linear parameter, internal pressure, isochoric thermo-acoustical parameter and isochoric temperature coefficient of internal pressure have also been calculated. The Moelwyn-Hughes parameter has been utilized to establish relation between the Bayer's non linear parameter, internal pressure and Sharma constant. Relationships among the isobaric, isothermal and isochoric thermo-acoustical parameter have been studied and analyzed for PAN/clay nano composites. The obtained results have been compared with the experimental results as available in literature. The non-ideal behavior of the polymer solution has been explained in terms of its composition and variation of its acoustical and thermo-dynamical parameters. The present treatment offers a convenient method to investigate thermo-acoustic properties and anharmonic behavior of the system under study.

Keywords: *Molecular interactions, Nanocomposites, Polymer solutions, Acoustical parameters, Non-linear parameters, anharmonic behavior*

Cite This Article: D. P. Singh, and Arun Upmanyu, "Acoustical Investigations of Molecular Interactions in Polymer Solution of Pan/Clay Nano Composites and Dmso." *Journal of Polymer and Biopolymer Physics Chemistry*, vol. 2, no. 4 (2014): 73-77. doi: 10.12691/jpbpc-2-4-3.

1. Introduction

Recently organic-inorganic nano-composites have attracted a great deal of attention in the materials science [1,2,3]. The polymers/clay nano-composites, with nano scale dispersion of the inorganic clay in the continuous polymer matrix, often exhibits enhanced material properties. The ultrasonic investigation of their solutions, prepared by dissolving these in a suitable solvent, indicates molecular interactions among the different constituents. In the present study several thermo-acoustic, thermo-dynamical and nonlinear parameters are determined for PAN/Cloisite ®30 nano-composites prepared with different clay content, and dissolved in DMSO at 30°C. Qualitative as well as quantitative information about the molecular interactions prevailing in these systems is obtained.

2. Theory

Using experimental data of ultrasonic velocity (U), density (d) and refractive index (n_D) taken from literature [3], several acoustical and thermo-dynamical parameters for the polymer solutions of PAN/ clay nano-composites and DMSO are determined. The standard relations as reported in literature [4,5,6], are used to evaluate isothermal compressibility (K_T), adiabatic compressibility (K_S), specific heat ratio (γ), volume expansivity (α), surface tension ($\sigma_{S.T.}$), intermolecular free length (L_f), specific sound velocity (r), specific adiabatic compressibility (w), pseudo Gruneisen parameter (Γ), classical absorption coefficient $(\alpha/f)^2$. Some thermo-elastic parameters such as longitudinal ultrasonic velocity (U_l), shear ultrasonic velocity (Us), Young's modulus (E), shear modulus (G), bulk modulus (K) and Poisson's ratio (σ) are also calculated. Non-linear parameters e.g. Moelwyn-Hughes parameter (C_1), reduced volume ($\tilde{V}$), reduced isothermal bulk modulus ($\tilde{\beta}$), Sharma's constants (S_0, S*, $S*_0$), Huggins parameter (F), isobaric acoustical parameter (K), isochoric acoustical parameter (K"), isothermal acoustical parameter (K') fractional free volume (f), repulsive exponent (n) thermo acoustical parameter such as (A*) and (B*), Bayer's non-linear parameter (B/A), internal pressure (Pi), and isochoric thermo acoustical parameter (δ) have been determined by using standard relations as available in literature [6].

3. Results and Discussion

Some of the theoretically evaluated thermo-acoustical, thermo-dynamical and non linear parameters for polyacrylonitrile (PAN) /clay nano composite solution in DMSO at 30°C and at various concentrations for the samples; virgin PAN (V) and PAN/Clay loaded samples; PNC1, PNC2 and PNC3 are reported in Tables 1-6. All the results are reported in SI units except stated otherwise.

A perusal of Table 1 indicates that K_s, K_T, ϒ and α, show regular decrease as the concentration of the PAN or PAN/clay nano-composite increases from 0.1 to 0.6 for each sample. These parameters also found to be having greater magnitude as compared to the solution of virgin PAN (V) at all concentrations. The decrease in the value of K_s and K_T confirms the lesser availability of the free volume and closer packing of the molecules, suggesting molecular association between the constituents of the polymer solution. The regular increase in the σ_{ST} with increase in the concentration of the solution confirms the existence of enhanced molecular interactions between the molecules of the interacting species and provide a quantitative knowledge about the strength of these. In Table 2 thermo-dynamical parameters such as L_f, *r, w, Γ*, $(\alpha/f)^2$ are reported. The steady decrease in L_f values with rise in concentration of the PAN/clay nano-composite increases from 0.1 to 0.6. This is in agreement with the above conclusion of enhanced molecular interactions among the solute and solvent particles.

Table 1. Some acoustical and thermo dynamical parameters for solution of PAN/Clay nano-composites in DMSO

Sample	Conc. %W/V	K_T × 1011	$K_S \times 10^{11}$	γ	$\alpha \times 10^3$	$\sigma_{S.T.}$
PAN(V)	0.1	5.85	4.43	1.3213	1.028	36.64
	0.2	5.81	4.40	1.3211	1.026	37.12
	0.4	5.68	4.30	1.3207	1.021	37.61
	0.6	5.58	4.22	1.3199	1.016	37.84
PNC1	0.1	6.02	4.53	1.3288	1.036	36.48
	0.2	5.96	4.49	1.3275	1.033	36.73
	0.4	5.82	4.39	1.3271	1.027	36.38
	0.6	5.70	4.31	1.3214	1.021	38.01
PNC2	0.1	6.09	4.58	1.3293	1.039	36.13
	0.2	6.00	4.52	1.3277	1.035	36.57
	0.4	5.82	4.39	1.3251	1.027	37.39
	0.6	5.73	4.33	1.3217	1.023	37.84
PNC3	0.1	6.14	4.61	1.3297	1.041	35.95
	0.2	6.01	4.52	1.3281	1.035	36.53
	0.4	5.87	4.43	1.3261	1.029	37.15
	0.6	5.77	4.36	1.3219	1.025	37.66

Table 2. Some thermo dynamical parameters for solution of PAN/Clay nano-composites in DMSO

Sample	Conc. % (W/V)	$r \times 10^{-5}$	$w \times 10^{-5}$	L_f (pm)	Γ	$(\alpha/f)^2 \times 1011$
PAN(V)	0.1	1064	2831	13.81	1.0307	1.17771
	0.2	1065	2832	13.77	1.0314	2.96189
	0.4	1068	2838	13.62	1.0363	8.19404
	0.6	1069	2841	13.49	1.0383	12.9637
PNC1	0.1	1082	2870	13.97	1.0472	1.09255
	0.2	1080	2865	13.91	1.0457	2.11241
	0.4	1083	2852	13.75	1.0403	4.65760
	0.6	1080	2843	13.63	1.0380	8.09945
PNC2	0.1	1081	2869	14.05	1.0457	1.11229
	0.2	1079	2864	13.95	1.0446	2.10613
	0.4	1077	2859	13.76	1.0441	4.58815
	0.6	1070	2842	13.67	1.0373	8.01583
PNC3	0.1	1081	2869	14.10	1.0459	1.09723
	0.2	1080	2867	13.96	1.0457	2.02611
	0.4	1079	2863	13.81	1.0452	4.48547
	0.6	1069	2841	13.71	1.0364	7.87401

The almost constant behavior of *r, w* is as expected. *Γ* shows a slight increase with increase of concentration in PAN (V) sample but it shows a regular decrease in its magnitude with rise in concentration in other samples. As *Γ* points to the existence of quasi-crystalline structure in the solution so it points to more stronger association in solute-solvent molecules in solutions containing PNC1, PNC2 and PNC3 sample as compared to the solutions containing PAN(V) sample. $(\alpha/f)^2$ reports a steady increase in its values in all samples under investigation. This trend of variation of $(\alpha/f)^2$ is due to the addition of the higher molar weight solute (PAN) leading to the greater denseness of the solution. The greater absorption of ultrasonic wave energy by a denser solution is as expected.

Table 3. Some elastic parameters for solutions of PAN/Clay nano-composites in DMSO

Sample	Conc. % (W/V)	U_l	U_S	$E \times 10^9$	$G \times 10^9$	$K \times 10^{10}$	σ
PAN(V)	0.1	6103	3920	39.64	16.72	11.89	0.1275
	0.2	6120	3999	39.89	17.03	11.96	0.1275
	0.4	6187	4043	40.80	17.42	12.24	0.1276
	0.6	6238	4077	41.56	17.74	12.47	0.1278
PNC1	0.1	6079	3967	38.68	16.46	11.60	0.1259
	0.2	6097	3989	39.01	16.70	11.70	0.1262
	0.4	6164	4032	39.92	17.08	11.98	0.1263
	0.6	6186	4049	40.73	17.44	12.22	0.1274
PNC2	0.1	6045	3946	38.19	16.27	11.46	0.1258
	0.2	6080	3979	38.78	16.60	11.63	0.1261
	0.4	6150	4024	39.91	17.08	11.97	0.1267
	0.6	6170	4036	40.48	17.31	12.14	0.1274
PNC3	0.1	6028	3935	37.94	16.17	11.38	0.1257
	0.2	6080	3979	38.74	16.59	11.62	0.1260
	0.4	6132	4012	39.58	16.94	11.88	0.1264
	0.6	6152	4036	40.23	17.22	12.07	0.1273

Table 4. Some non-linear parameters for solutions of PAN and PAN/Clay nano-composites in DMSO

Sample	Conc. % (W/V)	C1	$\overline{V}$	$\tilde{\beta}$	S_0	S*	S_0*
PAN(V)	0.1	7.9566	1.257	6.171	1.117	1.4157	1.1468
	0.2	7.9610	1.257	6.164	1.117	1.4150	1.1466
	0.4	7.9770	1.255	6.140	1.118	1.4127	1.1461
	0.6	7.9903	1.254	6.120	1.118	1.4107	1.1456
PNC1	0.1	7.9372	1.258	6.201	1.117	1.4186	1.1475
	0.2	7.9436	1.258	6.191	1.117	1.4176	1.1473
	0.4	7.9598	1.257	6.166	1.117	1.4152	1.1467
	0.6	7.9755	1.255	6.142	1.118	1.4129	1.1461
PNC2	0.1	7.9284	1.259	6.215	1.117	1.4199	1.1479
	0.2	7.9394	1.258	6.198	1.117	1.4183	1.1475
	0.4	7.9601	1.257	6.165	1.117	1.4152	1.1467
	0.6	7.9711	1.256	6.149	1.118	1.4135	1.1463
PNC3	0.1	7.9238	1.259	6.222	1.117	1.4206	1.1480
	0.2	7.9386	1.258	6.199	1.117	1.4184	1.1475
	0.4	7.9541	1.257	6.175	1.117	1.4160	1.1469
	0.6	7.9668	1.256	6.155	1.117	1.4142	1.1464

A perusal of Table 3 indicates that U_l, U_s, E, G, K and σ show slight but regular increase with increase in concentration from 0.1 to 0.6, for each sample solution. The increase in magnitude of these parameters is, due to the addition of PAN molecules (having higher molar weight) to the solution and also due to the enhanced molecular association among constituents of the solution, leading to the denseness of the system.

Several non-linear parameters such as C_1, $\overline{V}$, $\tilde{\beta}$, S_0, S^*, S^*_0, F, K, K'', K', f, η, α*, P_i, B/A, A^* and B^*, $(\tilde{T})$ and δ are presented in the Table 4 to Table 6. The perusal of Table 4 indicates that C_1 value varies 7.957 to 7.990 and 7.937 to 7.967 for virgin PAN and PAN/Clay composites respectively. This is in agreement with the value of the weakly-associated liquids as reported by Tiwari et al. [7] and lower than polymers as reported by Singh et al. [5,6]. This signifies the nonlinear variation of the volume expansivity of the system under investigations. The $\tilde{\beta}$ value range from 6.17 to 6.12 and 6.20 to 6.15 for virgin PAN and PAN/clay composites respectively. These values compare well with the $\tilde{\beta}$ values reported for molten alkali halides (~ 5 to 7) and polymers (~ 4 to 8). The result reported in Table 4 indicates that the value of the S_0 remains fairly constant within the acceptable range of experimental error. The estimated value of the S_0 in general lies in the range 1.11 ± 0.01 for all the samples under study. These values are in good agreement with results reported by Sharma [8-9]. The calculated value of S* are 1.41 ± 0.01 for all the samples as compared 1.15 for polymers as reported by Reddy et al. [10]. It is interesting to note that the value of S_o* is 1.15 for these samples and higher than that of polycrystalline solids.

Table 5. Some non-linear parameters for solutions of PAN and PAN/Clay nano- composites in DMSO

Sample	Conc.(%W /V)	F	K	$K^{//}$	$K^{/}$	f	N
PAN(V)	0.1	2.0741	3.4783	0.5781	4.0563	0.1978	15.338
	0.2	2.0749	3.4805	0.5772	4.0577	0.1977	15.346
	0.4	2.0774	3.4885	0.5740	4.0625	0.1975	15.375
	0.6	2.0794	3.4952	0.5714	4.0665	0.1974	15.399
PNC1	0.1	2.071	3.4686	0.5819	4.0505	0.1980	15.303
	0.2	2.0721	3.4718	0.5806	4.0524	0.1979	15.315
	0.4	2.0747	3.4799	0.5774	4.0573	0.1977	15.344
	0.6	2.0771	3.4878	0.5743	4.0621	0.1975	15.372
PNC2	0.1	2.0696	3.4642	0.5837	4.0478	0.1981	15.287
	0.2	2.0714	3.4697	0.5815	4.0512	0.1980	15.307
	0.4	2.0747	3.4801	0.5773	4.0574	0.1977	15.345
	0.6	2.0764	3.4856	0.5752	4.0607	0.1976	15.364
PNC3	0.1	2.0688	3.4619	0.5846	4.0465	0.1982	15.279
	0.2	2.0712	3.4693	0.5816	4.0509	0.1980	15.305
	0.4	2.0738	3.4771	0.5785	4.0556	0.1978	15.334
	0.6	2.0758	3.4834	0.5760	4.0594	0.1977	15.357

The result reported in Table 5 point out that the values of ‘F’ ranges from 2.074 to 2.079 and 2.071 to 2.076 for virgin PAN and PAN/ clay nano-composites respectively. These values are more than that observed for polymers, molten alkali halides, liquid alkali metals and ionic liquids as reported by Sharma [9]. The average value of ‘f’ for all the samples under study are found to be about 0.198 as compared to 0.20 for saturated hydrocarbons and about 0.15 for fluorocarbons. This points out that free volume values for theses samples, in the given concentrations range, are almost equal to the free volume values for saturated hydrocarbons but are slightly larger than that for fluorocarbons, as reported by Sharma [11]. The quasi constancy of ‘f’ at given temperature and concentrations range has significance in relation to the universal value of ‘f’ at the glass transition temperature Williams et. al. [12]. The average value of n found to be 15.37 and about 15.31 for virgin PAN and PAN/ clay composite respectively. These values of n have magnitude more than that reported by Saczkiewiez for polymers and fluorocarbons. The values of *K*, K’ and *K”* range from 3.46- 3.50; 4.0465-4.0665, and 0.571-0.581 for all the samples. The K’ and *K”* have recently been shown as an important factor which has a significant effect on the thermo acoustical properties of liquids fluorocarbons.

Table 6. Some non-linear parameters for solutions of PAN and PAN/Clay nano composites in DMSO

Sample	Conc. % (W/V)	A*	B*	B/A	$P_i \times 10^{-9}$	δ
PAN(V)	0.1	1.0488	1.0569	6.9566	5.323	0.2631
	0.2	1.0487	1.0568	6.9610	5.349	0.2632
	0.4	1.0486	1.0566	6.9770	5.441	0.2637
	0.6	1.0485	1.0565	6.9903	5.519	0.2641
PNC1	0.1	1.0489	1.0571	6.9372	5.213	0.2625
	0.2	1.0488	1.0570	6.9436	5.249	0.2627
	0.4	1.0487	1.0568	6.9598	5.342	0.2632
	0.6	1.0486	1.0566	6.9755	5.433	0.2636
PNC2	0.1	1.0489	1.0572	6.9284	5.163	0.2623
	0.2	1.0489	1.0571	6.9394	5.226	0.2626
	0.4	1.0487	1.0568	6.9601	5.344	0.2632
	0.6	1.0487	1.0567	6.9711	5.407	0.2635
PNC3	0.1	1.0490	1.0572	6.9238	5.138	0.2621
	0.2	1.0489	1.0571	6.9386	5.221	0.2626
	0.4	1.0488	1.0569	6.9541	5.309	0.2630
	0.6	1.0487	1.0567	6.9668	5.382	0.2634

The perusal of the Table 6 indicates that B/A show slight increase for the virgin PAN and PAN/clay composites. The increase in the values of B/A reports a decrease in the intermolecular modes of vibrations and anharmonicity in the samples under study. It also indicates the prevalence of associating tendencies and weak interaction in these samples. The average value of dimensional less parameters A^* and B^* are about 1.05 and 1.06 respectively. The values are in agreement with the corresponding value for fluorocarbons fluids. The δ values vary within 0.2621 to 0.2641. The increase in P_i value, with rise in concentration of solute for all the samples, points out to the specific orientation of the solvent molecules around the solute molecules. It is most likely due to the influence of electrostatics field of ions. This points out to the associating tendency of the molecules of PAN with chemical additives.

4. Conclusions

The trends of thermo-acoustical, thermo-dynamical and nonlinear parameters for the systems under study indicate the existence of enhanced molecular interactions between the molecules of the interacting species. The closer packing of the molecules and the existence of quasi crystalline structures in the solutions are pointed out. The trends of variations of various thermo-acoustic parameters, with increase in concentration of solute, point to the orientational adjustments of solvent molecules around solute molecules. The strength of the intermolecular interactions prevalent in the polymer solutions is aptly reflected in the magnitudinal variation of the parameters under investigation. It is pointed out that to describe the non linear behavior and anharmonic properties of the polymer/clay nano-composites solutions, ultrasonic velocity and volume expansivity data is of immense usage. It helps us to understand the effect of microscopic factors such as molecular order and intermolecular interactions upon the macroscopic behavior of such systems.

References

[1] G. Sanchez-Olivares, A. Sanchez-Solis, O. Manero. Burning rate, mechanical and rheological properties of HIPS-PET and clay nanocomposites. *Int. Jour. Polymer. Mater.*, 57 (5): 417, 2008.

[2] S. Maiti, N. Shrivastava, S. Suin and B. B. Khatua. Low percolation threshold in melt-blended PC/MWCNT nanocomposites in the presence of styrene acrylonitrile (SAN) copolymer: preparation and characterizations by synthetic metals. 165: 40, 2013.

[3] S. K. Swain and S. K. Patra. Ultrasonic and viscometric study of synthesized PAN/clay nanocomposites. *Int. J. of Polym. Mater*, 60: 559, 2011.

[4] A. Upmanyu and D. P. Singh. Ultrasonic studies of molecular interactions in polymer solution of the polyisobutylene and benzene. *Acta Acustica united with Acustica*, 100; 434, 2014.

[5] D. P. Singh and A. P. Singh. Acoustical investigations of chlorofluoroethyllene polymers, *Acustica*, 81; 177, 1995.

[6] D. P. Singh and Bhajan Singh. A study of thermo-acoustical parameters of some polymers. *Ind. J. Phys.* 66 A (5); 671, 1992.

[7] S. A. Tiwari and S. Rajgopalan. Thermo-acoustical parameters in ethyl and propyl benzoates at 228K-293K, *Acoust. Lett.,* 14; 92, 1992.

[8] B. K. Sharma. The relationship between the Grüneisen and other thermodynamic parameters and intermolecular forces in polymers. *Polymer*, 24; 314, 1983.

[9] B. K. Sharma. Isochoric temperature coefficient of surface tension and S_0-parametre of quasi-spherical molecular liquid. *Pramana*, 26; 223, 1986.

[10] R. R. Reddy and M. M. Murthty. Simple expressions for the Moelwyn-Hughes parameters and related thermo-acoustical parameters of polymers, *Acoust. Lett.,* 10; 128, 1987.

[11] B. K. Sharma. Thermo-acoustic and nonlinear properties of quasi spherical molecular liquids through internal pressure-temperature data. *J Pure & App. Phys.*, 23; 247, 1985.

[12] M. L. Williams, R. F. Landel and J. D. Ferry. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming Liquids. *J. Am. Chem. Soc.*, 77; 3701, 1995.