Dielectric relaxation in antiplasticized poly n-butyl methacrylate system

D. D. Deshpande and N. R. Kandasamy
Department of Chemistry, Indian Institute of Technology, Bombay-400 076, India
(Received 11 September 1980; revised 15 January 1981)

The dielectric $\alpha\beta$ relaxation process has been studied for poly n-butyl methacrylate (PBMA) in presence of various additives such as cholesteric liquid crystals and some isotropic liquids. Addition of isotropic liquids increased log (f_{max}) with increasing concentration at constant temperature and decreased the activation energy. The cholesteric liquid crystal additives, however, decreased log (f_{max}) and the free volume with increasing concentration at constant temperature. The data gathered were fitted to a master curve to evaluate the decay function, $\phi(t)$ and the parameter β. The normalized loss curves were found to be broadened with increased asymmetry both with isotropic and cholesteric liquid crystal additives. These studies clearly revealed the antiplasticization effect of some of the cholesteryl liquid crystal additives. The extent of broadening and the asymmetry of the loss curves cannot be explained on the basis of free volume theory alone and a mechanistic approach is used to explain the results. The values of $\Delta\beta/\Delta c$ have thus been explained on the basis of a gradient of the segments mobility leading to an increased spread of relaxation times.

INTRODUCTION

Antiplasticization has been inferred from the static or dynamic mechanical behaviour of polycarbonates, polysulphonates and chlorinated or nitrated diphenyl derivatives[1-4]. However, analogous dielectric behaviour has not been reported so far. Most of the earlier relaxation work on plasticized polymers involved the study of shape of the curves using the Cole–Cole[5] or the Cole–Davidson[6] parameter. It is argued by many authors that non-Debye behaviour is attributed to a non-exponential decay function for a cooperative relaxation process occurring in polymer systems[7-11]. However, the Cole–Cole, Cole–Davidson and Havriliak–Negami[12] functions have been successful in describing dielectric data. In the present work, we have studied the applicability of the time–temperature superposition principle to plasticized and antiplasticized systems and used the non-exponential decay function[8].

$$\varphi(t) = \exp(-t/\tau)^{\beta} \qquad (1)$$

where $0 < \beta \leqslant 1$.

EXPERIMENTAL

Poly n-butyl methacrylate, (PBMA) was prepared by the radical polymerization of n-butyl methacrylate monomer with benzoyl peroxide at $\sim 70^{\circ}$C. The number average molecular weight, as determined on a membrane osmometer was 120000. The cholesteric liquid crystals were prepared by the reaction of the appropriate acid chloride with cholesterol. The polymer films with the required amount of additives were prepared by solution casting over a clean mercury surface and drying in a vacuum oven $\sim 50^{\circ}$C for 3 to 4 weeks. The dielectric measurements were made on Rohde and Schwarz dielectric test bridge (VK 3520). A 3-electrode stainless steel cell of 10 cm diameter was designed for this purpose. The cell was placed in a thermostatically controlled oil bath and the temperature was maintained to within $\pm 0.05^{\circ}$C. The oscillator frequency was calibrated with a frequency counter for various ranges (30 Hz to 300 kHz).

RESULTS AND DISCUSSION

For each additive, three concentrations were studied. Readings were taken at closely spaced frequencies for each polymer film at four temperatures. Typical master plots of experimental points for PBMA pure and PBMA + cholesteryl benzoate are given in *Figure 1*. Plots of $\log_{10}(f_{max})$ vs. $(1/T)$ for different concentrations of PBMA, PBMA + cetyl acetate and PBMA + cholesteryl oleate are shown in *Figure 2* and these plots were used to evaluate the activation energy, ΔH_a. The maximum error in the values of ΔH_a is 1.5%. The shape of the normalized plots of $\varepsilon''/\varepsilon''_{max}$ against log (f/f_{max}) was evaluated from the normalized decay function[9]

$$\varphi(t/\langle\tau\rangle) = \frac{\int_{-\infty}^{+\infty} (\varepsilon''/\varepsilon''_{max})\cos\{(\omega/\omega_{max})(t/\langle\tau\rangle)\}\,\mathrm{d}\ln\log(\omega/\omega_{max})}{\int_{-\infty}^{+\infty} \varepsilon''/\varepsilon''_{max}\,\mathrm{d}\log(\omega/\omega_{max})} \qquad (2)$$

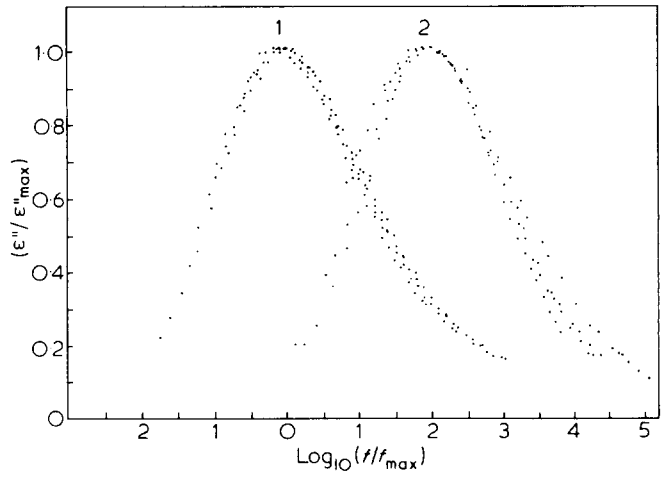

Figure 1 Plots of $(\epsilon''/\epsilon''_{max})$ *versus* $\mathrm{Log}_{10}(f/f_{max})$ for pure PBMA (1) and PBMA + cholesteryl benzoate (3.94%) (2). Curve (2) shifted two decades to right hand side for clarity

032-3861/81/091211-03$02.00

The evaluation of equation 2 was made by segmenting the normalized loss curve into five parts and fitting the low frequency end and the high frequency end (1st and 5th segments) to a third degree polynomial; the second and fourth segments were fitted to a first degree polynomial and the third segment was fitted to a second degree polynomial. The switch over points for the segments were selected carefully through one of the scope display programs which was developed solely* to evaluate equation 2 as accurately as possible[13]. The process of selecting switch over points and fitting the experimental data was continued until the best presentation of the experimental data was achieved. The coefficients of the fitted equations were used to represent $(\varepsilon''/\varepsilon''_{max})$ as a function of $\log(\omega/\omega_{max})$ for the evaluation of equation 2. The Romberg method of integration[14,15] was used with 2^{10} points for the values of $\log_{10}(t/\langle\tau\rangle)$ from -2.75 to $+3$ with an increment of 0.25. The lower limit of the integral was the lowest experimental value of $\log_{10}(f/f_{max})$ minus 0.25 units and the upper limit of the integral was the largest value of $\log_{10}(f/f_{max})$ plus 0.25 units. It was found that a range of not less than five decades was sufficient for the complete representation of the $\alpha\beta$ relaxation process.

* Programs were developed on varian 620/L computer with Mark II interface in Assembler and Fortran. Details would be available on request.

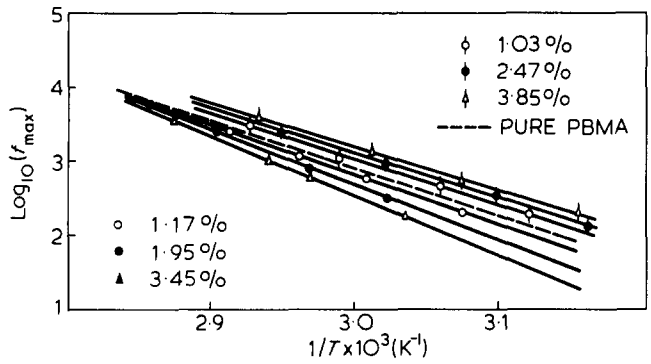

Figure 2 Plot of $\log_{10}(f_{max})$ *versus* $(1/T)$ for PBMA + cholesteryl oleate (○, ●, △) and PBMA + cetyl acetate (◇, ◆, △)

The result of change of activation energy and shifting of $\log_{10}(f_{max})$ with concentration (see *Table 1*) suggests that the additives fall into three different groups. The first group is the plasticizer group, isotropic liquids diphenyl ether and cetyl acetate which reduced the activation energy and hence increased the free volume. The second group is the antiplasticizers comprising of cholesterol and its esters of acetic, nanonoic, benzoic and oleic acids. These additives increased the activation energy and obviously reduced the free volume. Cholesteryl oleyl carbonate, cholesteryl 2-(ethoxy ethox) ethyl carbonate and a nematic liquid crystal, *N*-(*p*-methoxy benzylidine)-*p*-butylaniline (MBBA) form the third group which act as

Table 1 PnBMA + Additives: Smoothened data of $\log(f_{max})$ at 50°C, 60°C, 70°C, apparent activation energy ΔH_a, β and $(\Delta\log(f_{max})/\Delta c)$ and $\Delta\beta/\Delta c$

Sr. No. (1)	Additive (2)	Concentration (%) (3)	$\log(f_{max})$ 50°C (4)	60°C (5)	70°C (6)	t°C at which ϵ''_{max} occurs for 1 KHz (7)	$-\Delta H_a$ kcal mol^{-1} (8)	β (9)	$\frac{\Delta\log(f_{max})}{\Delta c}$ t = 60°C (10)	$\Delta\beta/\Delta c$ x 10 (11)
1	–	–	2.35	2.95	3.5	61.0	29.4	0.49		
2	Cholesterol	1.64	2.17	2.82	3.45	62.8	32.6	0.42		
		3.04	2.00	2.70	3.37	64.4	35.1	0.35	−0.10	−0.24
		3.58	1.75	2.60	3.30	65.5	39.5	0.58		
3	Cholesteryl	1.34	2.25	2.85	3.45	62.5	30.5	0.45		
	acetate	1.69	2.17	2.80	3.40	63.3	31.3	0.36	−0.085	−0.12
		3.02	2.05	2.70	3.35	64.5	33.2	0.24		
4	Cholesteryl	0.98	2.27	2.82	3.45	62.1	30.1	0.55		
	nanonoate	2.32	2.20	2.80	3.40	63.1	30.7	0.47	−0.028	−0.49
		4.21	2.10	2.75	3.35	64.1	31.0	0.39		
5	Cholesteryl	1.17	2.20	2.82	3.42	62.7	31.3	0.45		
	oleate	1.95	2.00	2.70	3.35	64.7	34.5	0.56	−0.12	−0.16
		3.45	1.82	2.55	3.25	66.1	36.4	0.49		
6	Cholesteryl	1.12	2.12	2.80	3.42	63.3	33.2	0.52		
	benzoate	2.01	1.87	2.62	3.35	65.1	37.7	0.42	−0.10	−0.41
		3.94	1.65	2.49	3.27	66.4	40.5	0.39		
7	Cholesteryl	1.61	2.46	3.02	3.55	59.6	27.8	0.52		
	oleyl carbonate	2.56	2.57	3.10	3.60	58.0	26.2	0.40	+0.12	−0.41
		3.41	2.72	3.22	3.70	55.5	24.9	0.27		
8	Cholesteryl	0.67	2.42	3.01	3.56	59.7	29.0	0.40		
	2-(ethoxy ethoxy)	2.62	2.52	3.10	3.64	58.2	28.5	0.36	+0.053	−0.06
	ethyl carbonate	3.83	2.67	3.17	3.70	56.6	26.2	0.38		
9	MBBA	1.25	2.57	3.10	3.60	58.1	26.1	0.38		
		2.42	2.75	3.22	3.70	55.2	23.1	0.37	+0.11	−0.01
10	Diphenyl	1.32	2.45	3.01	3.55	59.6	28.1	0.52		
	ether	2.56	2.55	3.08	3.60	58.5	26.8	0.43	+0.01	−0.80
		4.24	2.65	3.12	3.62	56.7	24.9	0.27		
11	Cetyl	1.03	2.45	3.07	3.57	59.3	28.7	0.49		
	acetate	2.47	2.57	3.12	3.65	57.7	27.5	0.45	+0.01	−0.03
		3.85	2.66	3.22	3.74	56.1	27.1	0.48		

plasticizers. It was expected that these two cholesteryl liquid crystals would act as antiplasticizers. But they did not fall in line with the other additives. This may be due to the low melting points compared with the range of temperatures at which the experiments were carried out.

It was necessary to examine the validity of the time-temperature superposition principle for the antiplasticized systems. Where the antiplasticization effect is greater, the tendency to form a good master curve was less. This can be seen from *Figure 1* where the pure PBMA curve gives a better master curve than PBMA + cholesteryl benzoate. This is because of the greater interaction of the additives with the polymer chains at lower temperatures than at higher temperatures where the segment mobility is considerably increased. This deviation is responsible for the less accurate master curve representation and the increased error in β to $\pm 5\%$.

It could be argued that the melting points of cholesterol and its esters were higher than the T_g of PBMA and that these additives would naturally exhibit such a behaviour. If the resultant T_g of the system follow the relation[16]

$$T_{g12} = T_{g1} w_1 + T_{g2} w_2 + k w_w w_2 \qquad (3)$$

where subscripts 1 and 2 stand for the additive and the polymer respectively, w's are the weight fractions and k is an empirical constant, the temperature at which the maximum loss occurred at a constant frequency should have increased with increase in melting point of the additive for a given concentration. It therefore follows that, the order in which the temperature at which loss maxima occur at a constant frequency, should have been: cholesterol (149) > cholesteryl benzoate (145) > cholesteryl acetate (115) > cholesteryl nanonoate (93) > cholesteryl oleate (44.5). The numbers in the paranthesis are the melting points. It can be clearly seen that, cholesteryl oleate, with the lowest transition temperature, behaved otherwise.

It is possible, as the measurement of temperature range was partly overlapping with the liquid crystalline temperature of cholesteryl oleate, that the mesophase caused alignment of polymer chains resulting in more efficient antiplasticization. Whether the system would have been in the liquid crystalline mesophase, needs a separate additional study. Another reason for the higher efficiency of cholesteryl oleate as an antiplasticizer could be that the oleate chain is less flexible due to the presence of a double bond.

PBMA, prepared by free radical polymerization at about 70°C was highly atactic and was confirmed from ^{13}C n.m.r. spectra. It is unlikely that a small percentage of additive would induce crystallization. Preliminary X-ray studies support this. If one looks for the characteristics for antiplasticizers and antiplasticizable polymers as described by Jackson and Cladwell[1-3], most of the points do not seem to be applicable to the present systems.

For a pure polymer, the loss curves become narrower at increased temperatures due to the increased free volume and increased segment mobility. From the free volume considerations, it therefore follows that a plasticizer should cause narrowing of the loss curves and make it more symmetrical. An antiplasticizer should behave in the opposite way. Qualitatively it could be seen that the plasticizers and antiplasticizers caused broadening and reduced the symmetry of the loss curves. For these systems β values are dimished as seen in *Table 1*.

Narrowing and more symmetrical loss curves would have shifted β towards unity, since β defines asymmetry as well as width of the curves. At lower concentrations of plasticizers, the mobility of segments in the immediate neighbourhood is increased and segments away from this core are unaffected, creating a gradient of segmental mobility, with varying relaxation times. In the case of antiplasticizer additives, the segments in the neighbourhood of the antiplasticizer molecules would be less mobile. Since this phenomenon will be applicable to any additive molecule, it is immaterial whether the additive is a plasticizer or an antiplasticizer; in both cases, spread of relaxation times and asymmetry of curves would probably be affected by causing reduction in the value of β. Even though the distribution of relaxation times need not necessarily represent the non-exponential decay function such as equation 1, it is convenient to visualize the polymer matrix with a gradient of segmental mobility due to the sparsely distributed additive molecules. A more detailed discussion is given by Williams[17].

The value of $\Delta\beta/\Delta c$ is negative for all the additives as they all caused broadening and asymmetry. Similar results were reported at even higher concentrations of the additives by Shears and Williams[18] for dibutyl phthalates-O-terphenyl systems. Baird and Sengupta[14] studied the effect of a large number of plasticizers and found that all of them broadened the loss curve and retained asymmetry.

CONCLUSIONS

The present dielectric studies reveal the antiplaxticizing effect of cholesteryl esters on PBMA. The free volume model alone is not adequate to describe the changes in the shape of the loss curves on addition of materials to a polymer, irrespective of whether the additive is a plasticizer or antiplasticizer. In both the types the additives cause broadening and this can be explained as due to an increased spread in relaxation times.

REFERENCES

1 Jackson, W. J. Jr. and Cladwell, J. R. *Adv. Chem. Ser.* 1965, **48**, 185
2 Jackson, W. J. Jr. and Cladwell, J. R. *J. Appl. Polym. Sci.* 1967, **11**, 217
3 Jackson, W. J. Jr. and Cladwell, J. R. *J. Appl. Polym. Sci.* 1967, **11**, 227
4 Robeson, L. M. and Faucher, J. A. *J. Appl. Polym. Sci.* 1972, **16**, 733
5 Cole, K. S. and Cole, R. H. *J. Chem. Phys.* 1941, **9**, 341
6 Davidson, D. W. and Cole, R. H. *J. Chem. Phys.* 1951, **19**, 1494
7 Davidson, D. W. *Can. J. Chem.* 1961, **39**, 571
8 Williams, G. and Watt, D. C. *Trans. Faraday Soc.* 1970, **66**, 80
9 Cook, M., Watt, D. C. and Williams, G. *Trans. Faraday Soc.* 1970, **66**, 2503
10 Williams, G., Watt, D. C., Dev, B. and North, A. M. *Trans. Faraday Soc.* 1971, **67**, 1323
11 Berbertan, J. G. and Cole, R. H. *J. Am. Chem. Soc.* 1968, **90**, 3100
12 Havriliak, S. and Negami, S. *J. Polym. Sci. (C)*, 1966, **14**, 99
13 Kandasamy, N. R. *PhD. Thesis*, Chemistry Department, I. I. T. Bombay (1980)
14 Baird, M. E. and Sengupta, C. R. *J. Chem. Soc. Faraday Trans. II*, 1974, **70**, 1741
15 Baird, M. E. and Sengupta, C. R. *J. Chem. Soc. Faraday Trans. II*, 1972, **68**, 1795
16 Jenkel, E. and Heusch, R. *Kolloid Z.* 1958, **130**, 89
17 Williams, G. *Chem. Rev.* 1972, **72**, 55
18 Shears, M. F. and Williams, G. *J. Chem. Soc. Faraday Trans. II*, 1973, **69**, 608