

Effect of Polar Solvents on Dynamic Moduli of Concentrated Solutions of Polyethylacrylate

N. NAKAJIMA, J. P. VARKEY

Institute of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301

Received 10 August 1997; accepted 22 November 1997

ABSTRACT: There have been many investigations on the effect of solvents on the dynamic moduli of concentrated polymer solutions. However, most of the polymers investigated were nonpolar, such as polystyrenes and polybutadienes. Moreover, the samples were usually model polymers of very narrow molecular weight distribution and were either linear or branched star. Our investigation was on a commercial polymer, which is polar and has long branches but is “gel free.” The solvents used were polar plasticizers. This study was motivated by the frequent observation that a small addition of plasticizers has little effect on the rubbery modulus or has an unexpectedly large reduction of the rubbery modulus, depending on a polymer–plasticizer pair. This work examines concentrated solutions of polyethylacrylate and three plasticizers (DBP, DHP, and DOP) at concentrations above 50% for DBP and DHP and above 80% for DOP. DOP did not dissolve the rubber at the lower concentrations. The temperature range was 30–150°C, and the frequency range was 10^{-2} – 10^2 rad/s. The time–temperature correspondence was applicable over the entire range of observation. The rubbery modulus was found to be independent of the plasticizer type at all concentrations. With dilution to 90% of polymer there was only small decrease of the modulus, and with further dilution the modulus decreased with a slope of 1.8 in the double-logarithmic plot of the modulus against concentration. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1727–1736, 1998

Key words: solvents; dynamic moduli; concentrated polymer solutions; polyethylacrylate

INTRODUCTION

Plasticizers are widely used in the polymer industries to tailor the processability and end use properties. The most well-known example is polyvinyl chloride (PVC) resin, which is softened by the addition of a plasticizer. Although rubber is a soft material, plasticizers are often used as a minor component. Sometimes a small amount of plasticizer causes a large drop in the rubbery modulus and other times only a small drop, depending

upon the polymer–plasticizer pair. In spite of rather frequent encounters, these observations are seldom pursued from the fundamental point of view. This work is a fundamental examination of the concentration dependence of dynamic moduli of rubber–plasticizer systems; the rubber is polyethylacrylate (ACM), an oil-resistant, high temperature resistant polymer and the plasticizers are a homologous series of phthalates.

There are a large number of studies in the literature on the concentration dependence of the dynamic moduli of polymer–solvent systems. The concentration dependence of the rubbery plateau modulus was found to obey a power-law relation,^{1–9}

Correspondence to: N. Nakajima.

Journal of Applied Polymer Science, Vol. 69, 1727–1736 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/091727-10

$$(G_N^0)_s = G_N^0(V_2)^n \quad (1)$$

where $(G_N^0)_s$ is the plateau modulus of the solution, G_N^0 is that of the undiluted polymer, and V_2 is the volume fraction of the polymer. In this relation there are no previously stated anomalies caused by a small addition of solvent (plasticizer). Moreover, the exponent is $n = 2.0\text{--}2.33$, which is thought to be a constant independent of the polymer and solvent type, whereas the anomalies are material dependent.

There are several possibilities that account for the discrepancy between the industrial observation and those in the literature. In the latter polymers were linear and had narrow molecular weight distribution. With a narrow distribution, an equal arm star gave $n = 1$.⁶ This implies that the exponent may be variable if the samples are mixtures of linear and star or of variable branch patterns. Also, these model polymers were nonpolar (i.e., polystyrenes and polybutadienes). Ferry reported that some polar polymers had very high values of the exponent n .¹⁰ Some commercial rubbers are polar, for example, nitrile butadiene rubber (NBR) and ACM. They often contain branched molecules, which vary in the degree of branching and the branch patterns. Nakajima and Okuno¹¹ found that the plateau modulus of an NBR dropped sharply upon a small addition of plasticizers and then decreased more slowly upon further dilution. Apparently, eq. (1) was not obeyed. In addition, the values of the plateau moduli depended upon the plasticizer, a better solvent giving a higher modulus.

In this work we chose another commercial rubber, ACM. The plasticizers are the same as the previous work.¹¹ Even though NBR and ACM are both polar, they are different in the following respect: the NBR is a copolymer containing 33% acrylonitrile, a polar comonomer, and 67% butadiene, a nonpolar comonomer, whereas the ACM is a homopolymer (except for a few percent of the cure-site comonomer). Another difference is the nature of the polymer chain. The ACM has 73% of its molecular weight as the pendant group. It is a relatively fat and short chain for a given degree of polymerization. The pendant group on the NBR is CN, which is smaller and exists less frequently along the chain. Both polymers are made via emulsion polymerization with a free-radical initiator. Therefore, they have a variable degree of long branching, resulting from a chain-transfer reaction.^{12,13}

EXPERIMENTAL

Samples

The rubber sample was polyethylacrylate supplied by Zeon Chemicals (HYTEMP 4051EP). It had a Mooney index of 40 at 100°C. It was a "gel-free" grade but contained 2.5% gel when measured through a Whatman no. 4 filter paper.

Plasticizers were DBP, DHP, and DOP. The plasticizers DBP and DOP were supplied by Harwick Chemical Corp. and DHP was supplied by Exxon Chemical Company.

Specimen Preparation

Concentrations of the polymer in the ACM-plasticizer mixtures were 100, 90, 80, 70, and 50% by weight for DBP and DHP and 100, 90, and 80% by weight for DOP. DOP did not dissolve the rubber at lower concentrations. Mixtures were prepared by placing the capped bottle containing the required amount of polymer and plasticizer into an oven at 60°C for 8 days. At this time the plasticizer was completely taken up by the rubber. The plasticizer-swollen rubber was gently pressed at 100°C into a thin sheet and then folded and repressed many times to ensure homogeneity. The weight was monitored to ensure no plasticizer loss. An internal mixer was not used, because it may cause a breakage of polymer chains and a change in entanglement density. A volatile cosolvent was not used for mixing because the removal of the solvent might not be complete or excessive drying might cause a loss of plasticizers.

A sheet of about 1.5–2.0 mm thickness was compression molded for 15 min at 115°C. A test specimen was diced from different parts of the mixture; then the reproducibility of the viscoelastic data, which included the homogeneity of the mixture, was examined.

Measurements

Dynamic Moduli of Undiluted Polymer and Concentrated Solutions

The measurements were performed with a Rheometrics mechanical spectrometer (RMS-800), using parallel plates of 25-mm diameter, in the oscillatory mode. The instrument calibration was double checked with a sample of silicone rubber (SE-30, General Electric). The reproducibility of the silicone calibration was within $\pm 2\text{--}3\%$. The linear viscoelastic response was observed by a

strain amplitude sweep that was made at a constant frequency of 10 rad/s in the shear strain amplitude of 0.005–0.10. All the data were taken at the strain amplitude of 0.03.

The temperature range was 30–150°C, and the measurements were taken at every 20°C. The frequency range was 10^{-2} – 10^2 rad/s. After loading the sample, 10–15 min was allowed for temperature equilibration. At each temperature the frequency sweep was made in the upswing from 10^{-2} to 10^2 rad/s and then the downswing. This was done to ensure that the sample did not undergo any chemical changes such as crosslinking or oxidation during the measurements. The samples tested at the lower temperature were taken out carefully to check the contact with the lower plate; if the contact was not proper, the test was repeated. The frequency upswing and downswing measurement at 175°C had a slight disagreement; hence, these data were not included for this study.

Density Measurement

The densities of the ACM mixtures were measured using a capillary rheometer (Monsanto processability tester). Mass flow rate and volume flow rate were measured at different temperatures to calculate the density of the ACM mixtures. A die having a diameter (D) of 0.0397 in. and a length/diameter ratio (L/D) of 30 : 1 was used for the experiment. The density was measured at different mass and volume flow rates and the plunger speed was found to have no effect on density. The purpose of making the density measurement was to see whether the magnitude of the modulus shift factor β_T agreed with the values of $\rho T/\rho_o T_o$ or not. Here ρ , T , and the subscript o denote density, temperature, and reference state, respectively.

RESULTS

The reproducibility of the data was examined with the undiluted ACM and other ACM mixtures at various temperatures. For the different specimens of the same mixture, it was possible to superpose the curves of log shear storage modulus, G' , or log shear loss modulus, G'' , as a function of log frequency by shifting along the modulus axis only. This indicates that the error was primarily in the modulus axis.

The data for the undiluted rubber fell within $\pm 5\%$ of the average of four runs at 110°C. The mixtures were prepared by repeated pressing, but the undiluted rubber was pressed only once before testing. To duplicate the same condition, undiluted rubber was pressed many times to see whether the mixing procedure altered the rubber or not. The data fell within $\pm 5\%$ of the average of the single-pressed undiluted rubber, indicating that the repeated pressing did not alter the rubber.

The homogeneities of the ACM mixtures were checked by testing different specimens of the same mixture. The reproducibility of the 90–10 (rubber–plasticizer) mixture was within $\pm 4\%$, the 80–20 mixture was within $\pm 3\%$, and the 70–30 mixture was within $\pm 6\%$ for all the frequencies tested at 150°C. The 50–50 mixture at 150°C was the lowest polymer concentration and the highest temperature of this work, hence, the moduli was lowest and the equipment response was weakest. Even at this condition the reproducibility was within $\pm 9\%$ at the lower frequencies.

The time–temperature superposition was performed in the following sequence in order to obtain the time shift and modulus shift independently so that the error in the modulus shift and that in the time shift would not influence each other. First a curve of $\log \tan \delta$ versus $\log \omega$ at each temperature was prepared. From the superposition of these curves along the frequency axis the time shift, α_T , was obtained because in $\tan \delta$ the modulus shift cancels out. After the α_T evaluation, a plot of $\log |G^*|$ versus $\log \omega \alpha_T$ was prepared for the data at each temperature. These curves were superposed along the modulus axis to obtain the modulus shift, β_T . The values of the time shift α_T and β_T are given in Tables I–III. The magnitudes of β_T were in agreement with the measured values of $\rho T/\rho_o T_o$ within $\pm 10\%$, as is evident from Table IV.

The results of the time–temperature superposition for ACM-DHP is shown in Figure 1(a) and (b), and the reference state was 90°C. The ACM-DBP and ACM-DOP system had similar results. With 100% ACM and all ACM–plasticizer mixtures, a good time–temperature superposition was obtained.

The time–concentration superposition was performed in the following sequence. Plots of $\log \tan \delta$ versus $\log \omega \alpha_T$ as shown in Figure 2 were shifted along the $\omega \alpha_T$ axis to match the rubbery region of the data. The magnitude of the shift was α_C . Then plots of $\log G'/\beta_T$ versus $\log \omega \alpha_T \alpha_C$ were

Table I Shift Factor α_T for Temperature Superposition

Sample		α_T at Temperature ($^{\circ}\text{C}$)						
Component	ACM Wt (%)	30	50	70	90	110	130	150
ACM	100	4.41×10^2	3.30×10^1	4.52×10^0	1	3.01×10^{-1}	1.17×10^{-1}	5.78×10^{-2}
ACM-DBP	90	2.10×10^2	2.20×10^1	3.78×10^0	1	3.71×10^{-1}	1.67×10^{-1}	9.22×10^{-2}
	80	1.06×10^2	1.51×10^1	3.22×10^0	1	4.15×10^{-1}	2.45×10^{-1}	1.49×10^{-1}
	70	6.29×10^1	1.10×10^1	2.85×10^0	1	4.91×10^{-1}	3.10×10^{-1}	2.29×10^{-1}
ACM-DHP	50	2.86×10^1	6.90×10^0	2.35×10^0	1	5.31×10^{-1}	4.20×10^{-1}	3.10×10^{-1}
	90	2.41×10^2	2.32×10^1	3.97×10^0	1	3.35×10^{-1}	1.37×10^{-1}	7.28×10^{-2}
	80	1.31×10^2	1.64×10^1	3.40×10^0	1	3.65×10^{-1}	1.75×10^{-1}	1.14×10^{-1}
ACM-DOP	70	8.34×10^1	1.36×10^1	3.12×10^0	1	3.99×10^{-1}	1.96×10^{-1}	1.15×10^{-1}
	50	4.21×10^1	8.81×10^0	2.60×10^0	1	4.61×10^{-1}	2.30×10^{-1}	1.78×10^{-1}
	90	2.73×10^2	2.45×10^1	4.00×10^0	1	3.30×10^{-1}	1.35×10^{-1}	6.87×10^{-2}
	80	1.61×10^2	1.90×10^1	3.58×10^0	1	3.50×10^{-1}	1.53×10^{-1}	8.04×10^{-2}
	70	1.13×10^2	1.56×10^1	3.34×10^0	1	3.84×10^{-1}	1.73×10^{-1}	9.98×10^{-2}

prepared. These plots are shown in Figure 3 for ACM-DBP, ACM-DHP, and ACM-DOP. From these plots the modulus shift (β_C) in the concentration superposition was found by shifting along the G'/β_T axis. The shift factors α_C and β_C are shown in Table V.

The results of the time–concentration superposition are shown for G' in Figure 4 for ACM-DBP, ACM-DHP, and ACM-DOP. At higher frequencies (i.e., the rubbery region) the concentration superposition is applicable whereas at the lower frequencies (i.e., the flow region) the moduli decreased with the increase in plasticizer concentration.

Table II WLF Constants C_1 and C_2

Sample	ACM Wt (%)	C_1	C_2
100% ACM	100	4.67	163.20
ACM-DBP	90	3.77	153.89
	80	2.78	136.27
	70	2.12	120.44
	50	1.56	113.40
ACM-DHP	90	4.23	160.81
	80	3.37	147.83
	70	2.82	134.10
ACM-DOP	50	2.50	132.33
	90	4.39	165.35
	80	4.30	174.03
	70	3.83	166.44

The modulus shift (β_C) evaluated from G' data was used to perform the concentration superposition for G'' . The results are shown in Figure 5 for ACM-DBP, ACM-DHP, and ACM-DOP. The curves did not superpose at the higher frequencies and at the lower frequencies. At the higher frequencies the deviation was a result of the decrease of time range for the rubbery region upon dilution. At the lower frequencies the deviation was similar to that observed with G' data. This indicated the effect of the decrease of the entanglement density on the long relaxation times.

DISCUSSION

The G' curves and G'' curves show two significant differences between ACM–plasticizer [Fig. 1(a,b)] and NBR–plasticizer¹¹ systems [Fig. 1(c)]. One is that with the ACM the time–temperature superposition was achieved, but with the NBR it was not. In the latter the moduli of the low frequency region decreased with the increasing temperature. This indicated a decrease of the solvent power with increasing temperature, resulting in the decrease of entanglement density. The polymer–solvent interaction between ACM and the plasticizers may not be very temperature sensitive in the temperature range. There may be an additional reason as stated below. The other difference is in the slope of the curves at the lowest frequency region. The ACM curves point down-

Table III Shift Factor and β_T for Temperature Superposition

Sample		β_T at Temperature ($^{\circ}\text{C}$)						
Component	ACM Wt (%)	30	50	70	90	110	130	150
ACM	100	6.52×10^{-1}	8.05×10^{-1}	9.20×10^{-1}	1	1.09×10^0	1.18×10^0	1.27×10^0
ACM-DBP	90	7.75×10^{-1}	8.44×10^{-1}	9.27×10^{-1}	1	1.08×10^0	1.15×10^0	1.23×10^0
	80	7.75×10^{-1}	8.41×10^{-1}	9.25×10^{-1}	1	1.08×10^0	1.18×10^0	1.28×10^0
	70	7.92×10^{-1}	8.56×10^{-1}	9.19×10^{-1}	1	1.08×10^0	1.18×10^0	1.29×10^0
	50	7.63×10^{-1}	8.39×10^{-1}	9.28×10^{-1}	1	1.08×10^0	1.16×10^0	1.28×10^0
ACM-DHP	90	7.89×10^{-1}	8.56×10^{-1}	9.21×10^{-1}	1	1.08×10^0	1.16×10^0	1.24×10^0
	80	7.99×10^{-1}	8.52×10^{-1}	9.31×10^{-1}	1	1.08×10^0	1.16×10^0	1.24×10^0
	70	8.00×10^{-1}	8.52×10^{-1}	9.25×10^{-1}	1	1.08×10^0	1.17×10^0	1.37×10^0
	50	7.60×10^{-1}	8.33×10^{-1}	9.25×10^{-1}	1	1.08×10^0	1.18×10^0	1.24×10^0
ACM-DOP	90	8.12×10^{-1}	8.74×10^{-1}	9.31×10^{-1}	1	1.07×10^0	1.13×10^0	1.20×10^0
	80	7.69×10^{-1}	8.38×10^{-1}	9.29×10^{-1}	1	1.07×10^0	1.13×10^0	1.17×10^0
	70	7.79×10^{-1}	8.55×10^{-1}	9.24×10^{-1}	1	1.08×10^0	1.14×10^0	1.21×10^0

ward with the increasing slope, a fact commonly observed in the flow region. The NBR curves are concave upward. This is caused by the entanglement involving giant molecules with multi-branches (gels). Both the ACM and the NBR contain a few percent of gel. Because both polymers were made via emulsion polymerization using a free radical initiator, the branch pattern of the gels must be similar. The critical difference is in the shape of the chains: ACM is a relatively fat and short whereas NBR is long and slender. The branches of the gels in ACM must be short enough to slip out easily in the flow region but those in NBR act as constraints against flow.

From α_T values the WLF constants,¹⁰ C_1 and C_2 were calculated and are listed in Table II. Then, from C_1 and C_2 , the free volume fraction, f_o , and the thermal expansion coefficient, α_f , were calculated as relative measures:

$$f_o = B/2.303C_1 \quad (2)$$

$$\alpha_f = B/2.303C_1C_2 \quad (3)$$

The concentration dependence of these parameters for ACM-DBP were found to be

$$f_o/B = -0.37V_2 + 0.454 \quad (4)$$

Table IV Density Measurement Results and Comparison with b_T from Time-Temperature Superposition

Sample Type	Temperature ($^{\circ}\text{C}$)	Plunger Speed (mm/min)	Mass Collected (g)	Time of Collection (s)	Volumetric Flow Rate (cm^3/s)	Mass Flow Rate (g/s)	Density (g/cm^3)	Actual $\rho T/\rho_o T_o$	β_T
100%	50	0.05	1.2145	180	0.3619	0.4048	1.1183	0.8906	0.805
100%	90	0.48	1.2943	20	3.4749	3.8829	1.1173	1	1
100%	150	2.70	3.5173	10	19.5468	21.1038	1.0796	1.1259	1.27
10% DHP	70	0.20	1.5798	60	1.4479	1.5798	1.0910	0.9473	0.921
10% DHP	90	0.35	1.3788	30	2.5533	2.7576	1.0883	1	1
20% DHP	50	0.15	1.1975	60	1.0859	1.1975	1.1027	0.9196	0.852
20% DHP	90	0.55	2.1241	30	3.9817	4.2482	1.0669	1	1
30% DHP	70	0.20	1.5393	60	1.4479	1.5393	1.0631	0.9662	0.925
30% DHP	90	0.55	3.4496	50	3.9817	4.1395	1.0396	1	1

The density of 100% ACM is $1.12 \text{ g}/\text{cm}^3$ at 25°C .¹⁴

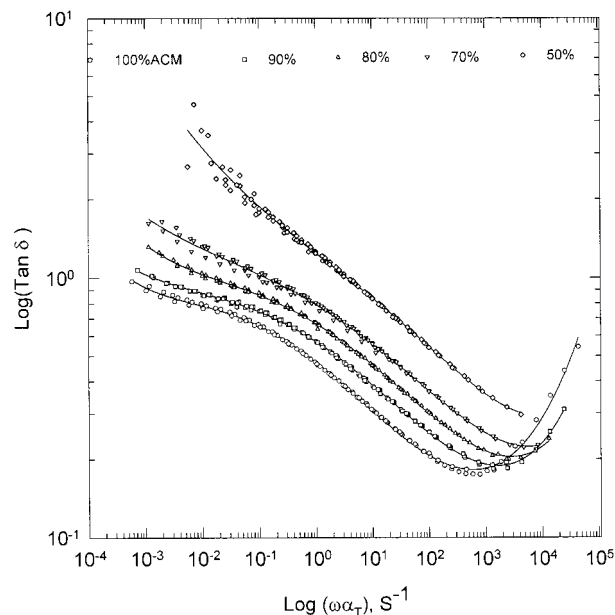
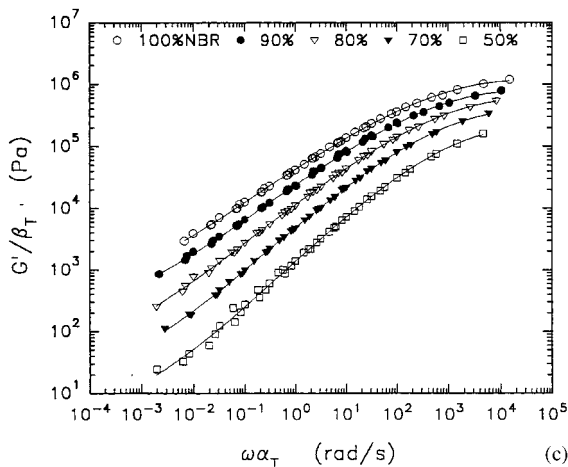
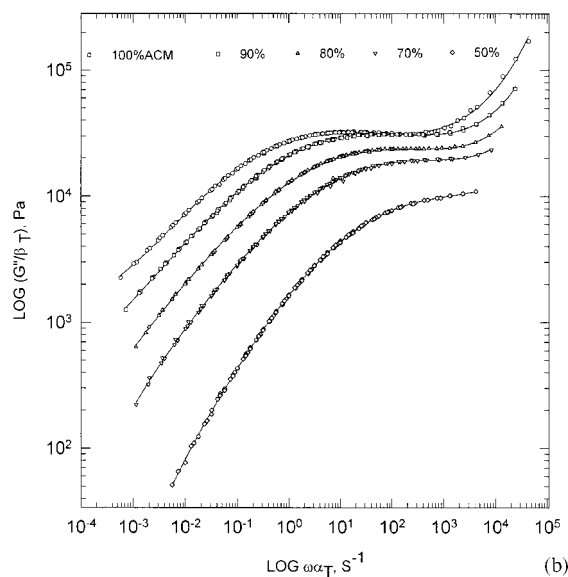
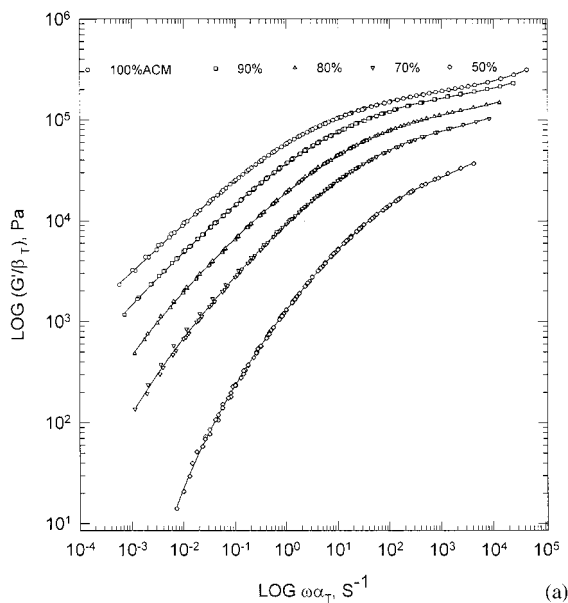


Figure 2 Plot of $\log(\tan \delta)$ versus $\log(\omega\alpha_T)$ for ACM-DHP systems: (○) 100% ACM, (□) 90% ACM-DHP, (△) 80% ACM-DHP, (▽) 70% ACM-DHP, and (◇) 50% ACM-DHP.

$$\alpha_f/B = -3.80V_2 + 4.25$$

for ACM-DHP:

$$f_o/B = -0.16V_2 + 0.256 \tag{5}$$

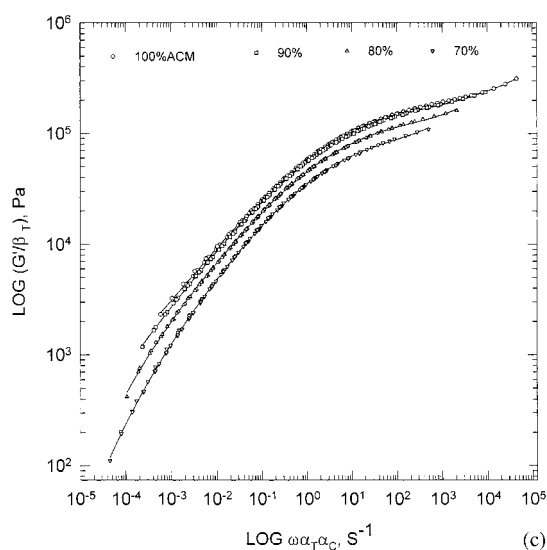
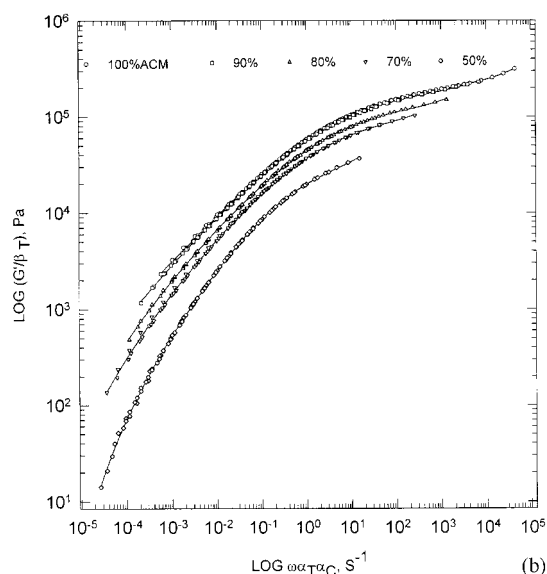
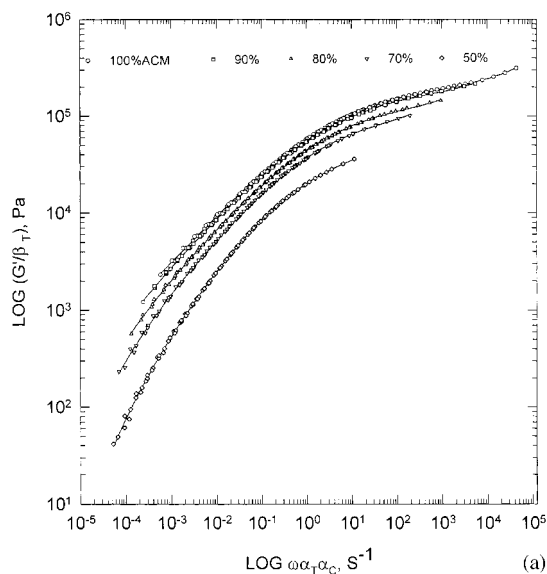
$$\alpha_f/B = -1.45V_2 + 2.01$$

and for ACM-DOP:

$$f_o/B = -0.057V_2 + 0.149 \tag{6}$$

$$\alpha_f/B = -2.86V_2 + 8.46$$

Figure 1 Results of time-temperature correspondence of (a) storage modulus for ACM-DHP systems: (○) 100% ACM, (□) 90% ACM-DHP, (△) 80% ACM-DHP, (▽) 70% ACM-DHP, and (◇) 50% ACM-DHP; (b) loss modulus for ACM-DHP systems: (○) 100% ACM, (□) 90% ACM-DHP, (△) 80% ACM-DHP, (▽) 70% ACM-DHP, and (◇) 50% ACM-DHP; and (c) storage modulus for NBR-DHP systems: (○) 100% NBR, (●) 90% NBR-DHP, (▽) 80% NBR-DHP, (▼) 70% NBR-DHP, and (□) 50% NBR-DHP.¹¹



As stated earlier, the observed values of β_T agree with those calculated from density and temperature.

Because the time–concentration superposition is applicable only in the rubbery region, the ensuing discussion on α_C and β_C is pertinent to the behavior of the rubbery region only. The following relation was found in α_C :

$$\log \alpha_C = a + bV_2 \quad (7)$$

or

$$-\log \alpha_C = bV_1 \quad (8)$$

because at $V_2 = 1$, $\log \alpha_C = 0$. The value of b is 4.61 for the ACM-DBP system, 4.58 for the ACM-DHP, and 4.07 for the ACM-DOP. The values of b are positive, because $\log \alpha_C$ is negative as shown in Table V. As V_1 increases, the value of $-\log \alpha_C$ increases. Therefore, the value of b , analogous to the effect of free volume on the time–temperature superposition, is a measure of facilitating the motion of the chain with dilution. As may be expected, the b value is larger for the lower molecular weight plasticizer.

The modulus shift (β_C) is a relative measure of the plateau modulus in which 100% ACM is taken as the reference. Figure 6 is a double logarithmic plot of β_C versus the volume fraction of the polymer V_2 . Apparently, the relation given by eq. (1) was not obeyed. Also, the plateau modulus is a function of concentration only and is independent of the plasticizer type.

The magnitude of plateau modulus is a function of entanglement density.¹⁰ In a better solvent the polymer chain is more extended, resulting in a higher entanglement density and giving a higher plateau modulus. Because the plateau modulus is found to be independent of the solvent type, these plasticizers for the ACM must be neutral solvents. Many investigators have reached a

Figure 3 Results of applying concentration shift factor, α_C , to time–temperature correspondence of storage modulus for (a) ACM-DBP systems: (○) 100% ACM, (□) 90% ACM-DBP, (△) 80% ACM-DBP, (▽) 70% ACM-DBP, and (◇) 50% ACM-DBP; (b) ACM-DHP systems: (○) 100% ACM, (□) 90% ACM-DHP, (△) 80% ACM-DHP, (▽) 70% ACM-DHP, and (◇) 50% ACM-DHP; and (c) ACM-DOP systems: (○) 100% ACM, (□) 90% ACM-DOP, (△) 80% ACM-DOP, and (▽) 70% ACM-DOP.

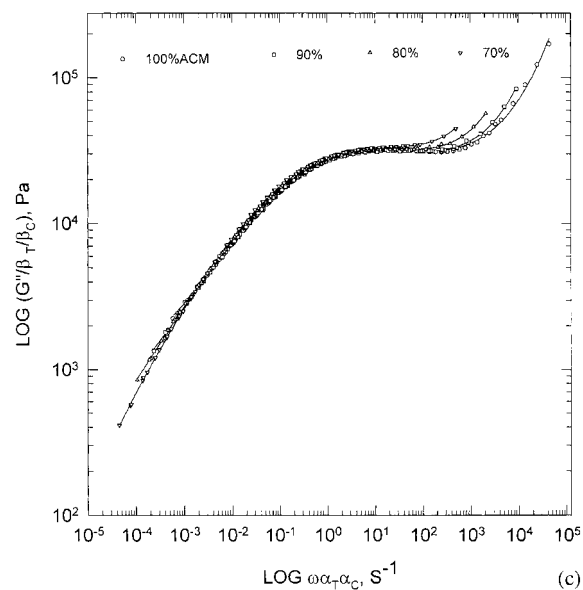
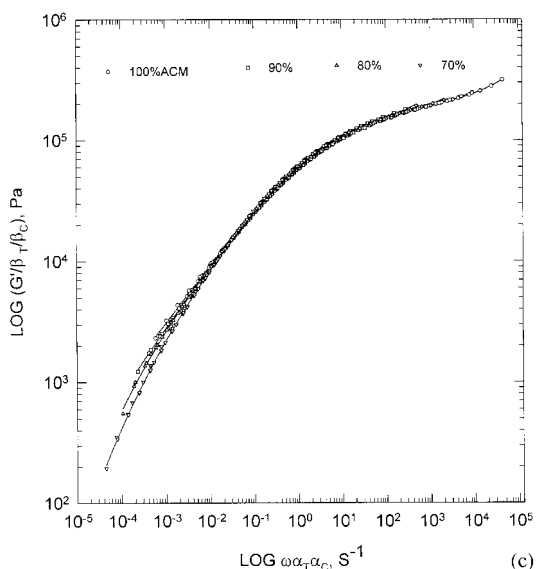
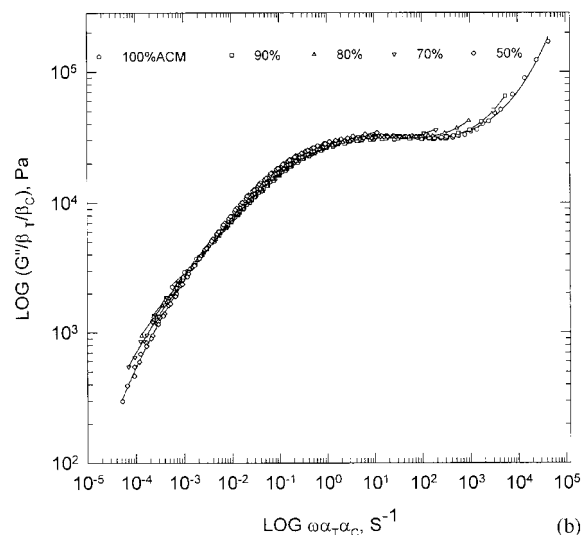
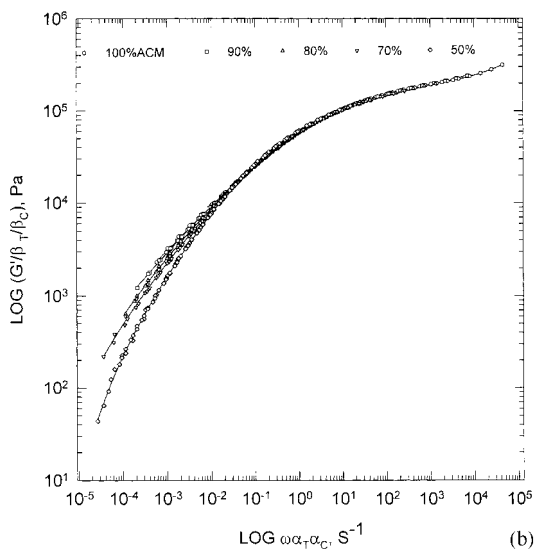
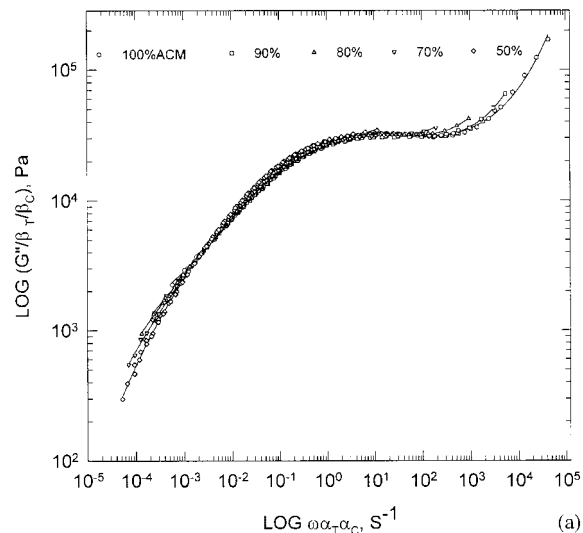
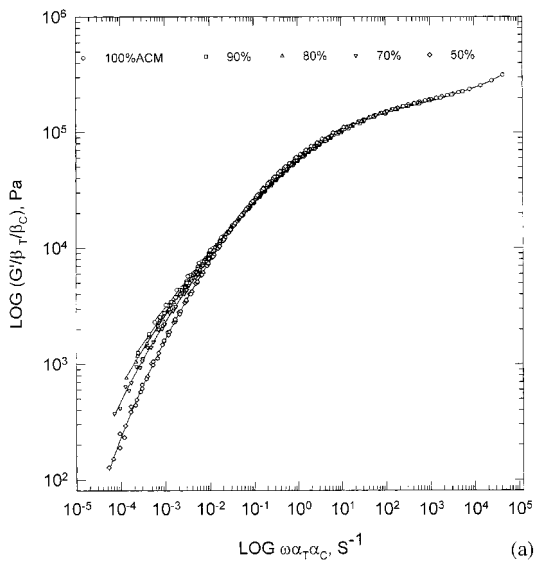


Figure 4 Results of time–concentration correspondence of storage modulus for (a) ACM-DBP systems, (b) ACM-DHP systems, and (c) ACM-DOP systems. Reference state: 100% ACM at 90°C.

Figure 5 Results of time–concentration correspondence of loss modulus for (a) ACM-DBP systems, (b) ACM-DHP systems, and (c) ACM-DOP systems. Reference state: 100% ACM at 90°C.

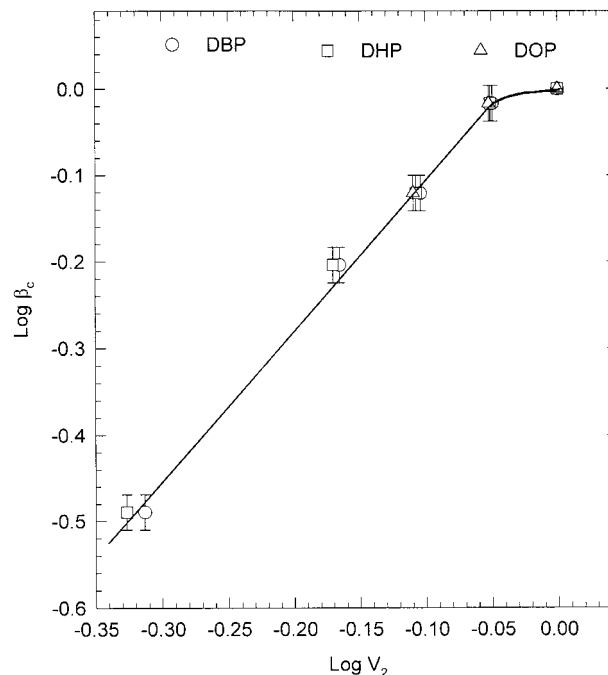
Table V Shift Factors α_C and β_C for Concentration Superposition

Sample			
Component	ACM Wt (%)	α_C	β_C
ACM	100	1	1
ACM-DBP	90	2.61×10^{-1}	9.62×10^{-1}
	80	8.85×10^{-2}	7.57×10^{-1}
	70	3.09×10^{-2}	6.25×10^{-1}
	50	3.98×10^{-3}	3.24×10^{-1}
ACM-DHP	90	2.89×10^{-1}	9.62×10^{-1}
	80	1.02×10^{-1}	7.57×10^{-1}
	70	3.15×10^{-2}	6.25×10^{-1}
	50	3.63×10^{-3}	3.24×10^{-1}
ACM-DOP	90	3.35×10^{-1}	9.62×10^{-1}
	80	1.30×10^{-1}	7.57×10^{-1}
	70	4.42×10^{-2}	5.69×10^{-1}

similar conclusion with a number of model polymers that are nonpolar and have very narrow molecular weight distributions.¹⁻⁹ However, this result is different from the observation of Nakajima and Okuno¹¹ in their work on NBR-plasticizer systems.

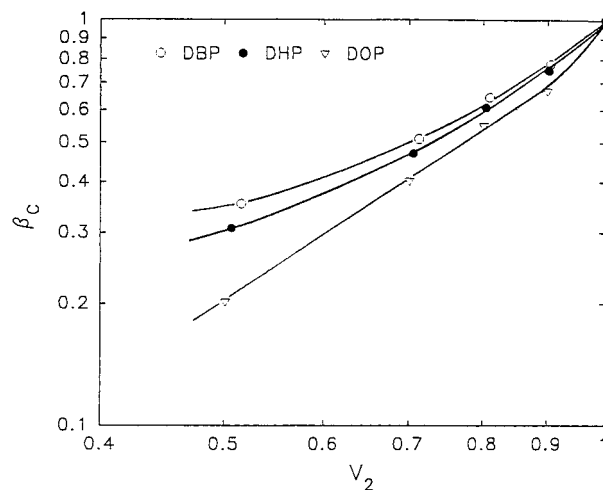
In Figure 6 the rubbery modulus is shown to decrease very little upon a 10% addition of the plasticizers. A further addition of the plasticizer causes the rubbery modulus to decrease with a slope of 1.8. Figure 7 shows a similar plot for NBR-plasticizer systems.¹¹ A sharp decrease in modulus occurs initially and then a gradual decrease occurs upon further dilution.

The difference between ACM and NBR systems with small additions of solvents (plasticizers) may be interpreted on the basis of polymer-polymer interaction (2,2) and polymer-solvent interaction (1,2). With ACM the 2,2 interaction is stronger than and relatively favored over the 1,2 interaction. The ACM rubbers are known to exhibit a strain-induced association upon large extension, a behavior similar to the strain-induced crystallization.¹⁵⁻¹⁷ This fact also implies the strong 2,2 interaction. The nature of the polar groups and the structure of the homopolymer have something to do with the observation. With NBR systems the 1,2 interaction is favored over the 2,2 interaction. In NBR, a copolymer from polar and nonpolar monomers, the 2,2 interaction may be more easily replaced by the 1,2 interaction.

**Figure 6** Plot of β_C versus V_2 for ACM-plasticizer systems: (○) DBP, (□) DHP, and (△) DOP. Reference state: 100% ACM at 90°C.

CONCLUSION

The rubbery plateau modulus of ACM dropped only by a small amount upon addition of plasticizers up to around 10% dilution. Further dilution caused the drop in plateau modulus at a slope less than 2.

**Figure 7** Plot of β_C versus V_2 for NBR-plasticizer systems: (○) DBP, (●) DHP, and (▽) DOP. Reference state: 100% NBR at 90°C.

The plateau modulus of NBR dropped sharply upon a small addition of plasticizers and then decreased more slowly upon further dilution.

The plateau modulus of ACM was independent of the type of plasticizers. The plateau modulus of NBR was dependent on the type of plasticizers.

The ACM, NBR, and plasticizers used were all polar. The above stated difference in the behavior of ACM and NBR systems might be explained in terms of the difference in the shape of the chain, polymer–polymer (2,2), and solvent–polymer (1,2) interactions. In the case of ACM systems the 2,2 interaction is stronger than and relatively favored over the 1,2 interaction. With the NBR systems the 1,2 interaction is favored over the 2,2 interaction. Also, another major difference that could contribute to the above observed behavior is the fact that the ACM chain is relatively fat and short compared to NBR for the same degree of polymerization.

The simple power law relation on the concentration dependence of plateau modulus that holds true for linear, narrow molecular weight distribution, nonpolar (model) polymers does not necessarily hold true for nonmodel polymers.

For the ACM system the concentration shift factor (α_C) has a simple linear relationship to the volume fraction of the polymer with the constant of proportionality different for different plasticizers.

This article was presented at the 151st Meeting of the Rubber Division of the American Chemical Society in Anaheim, CA, on May 6–9, 1997.

REFERENCES

1. N. Nemoto, T. Ogawa, H. Odani, and M. Kurata, *Macromolecules*, **5**, 641 (1972).
2. T. Masuda, N. Toda, Y. Aoto, and S. Onogi, *Polym. J.*, **3**, 315 (1972).
3. Y. Isono, T. Fujimoto, N. Takeno, H. Kajiura, and M. Nagasawa, *Macromolecules*, **11**, 888 (1978).
4. D. J. Plazek, E. Riande, H. Markovitz, and N. Raghupathi, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 2189 (1979).
5. G. Marin, E. Menezes, V. R. Raju, and W. W. Graessely, *Rheol. Acta*, **19**, 462 (1980).
6. V. R. Raju, E. V. Menezes, G. Marin, W. W. Graessely, and L. J. Fetters, *Macromolecules*, **14**, 1668 (1981).
7. J. E. Roovers, *Polym. J.*, **18**, 153 (1986).
8. R. H. Colby, L. J. Fetters, W. G. Funk, and W. W. Graessely, *Macromolecules*, **24**, 3873 (1991).
9. W. W. Graessely and S. F. Edwards, *Polymer*, **22**, 1329 (1981).
10. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, 1980.
11. N. Nakajima and S. Okuno, *J. Rheol.*, **38**, 541 (1994).
12. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, Chap. 9.
13. W. O. Baker, *Rubber Chem. Technol.*, **22**, 935 (1949).
14. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Wiley, New York, 1989.
15. N. Nakajima, C. D. Huang, J. J. Scobbo, Jr., W. J. Shieh, and H. R. Harrell, *Rubber Chem. Technol.*, **62**, 343 (1989).
16. N. Nakajima, J. J. Scobbo, Jr., and H. R. Harrell, *Rubber Chem. Technol.*, **60**, 742 (1987).
17. N. Nakajima and S. K. Sundarapandian, *Rubber World*, **212**, 41 (1995).