Viscoelastic Characterization of PVC Plastisol Melts for Foam Applications*

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Synopsis

Melt rheology and its time-temperature dependence have long been known to be fundamental properties associated with satisfactory expansion characteristics in vinyl foam. Since much is known about the relationship between rheology and material variables like polymer morphology and system composition, adequate rheological characterization should be quite helpful in polymer design and plastisol compounding.

Earlier attempts to study the melt rheology of plasticized PVC foam systems were only partially successful because instrument limitations required that the material be studied at too high shear rate or temperature, or that behavior of specific compositions be extrapolated from data obtained at considerably higher plasticizer level.

This paper deals with measurement of the viscoelastic behavior of melts from actual azodicarbonamide foam compositions. The Rheometrics Mechanical Spectrometer was used in the orthogonal mode to study both elastic modulus and loss modulus (viscosity) in the range of shear rates and temperatures which actually occur during commercial utilization of PVC foam compounds. The effects of changing vinyl resin types and plasticizer types and levels were explored.

INTRODUCTION

Most vinyl foams are made by melt expansion of PVC plastisols with nitrogen gas provided by thermal decomposition of azodicarbonamide. Such foams are fabricated as sheet goods and as an integral part of coatings for upholstery fabric, roll goods flooring, and shoe upper material. Typical processes operate at 180° to 210°C, and expansion is completed in 2 to 10 minutes. The rate of expansion and resistance to cell coalescence and collapse are important processing characteristics. The cell size, shape, and uniformity are important finished foam properties deriving from structure, as in the density. While it is possible to measure these parameters under controlled conditions and thus characterize materials such as PVC resins, plasticizers, blowing agents, and surfactants used in plastisol compounding, the result is empirical, and no fundamental understanding of the relationship between composition and processability results.

Phenomenologically and through extension of the theories of foaming,[1] it appears that surface energy, surface rheology, bulk rheology, rate of gas generation and diffusion, solubility of materials, and the characteristics of any

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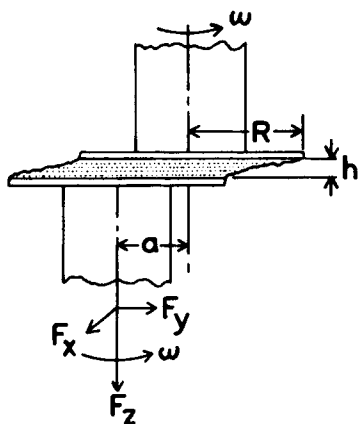
Fig. 1. Flow between eccentric rotating discs in Rheometrics Mechanical Spectrometer (orthogonal mode).

nucleating ingredients are important to foaming behavior. This work is intended to characterize the effect of one fundamental property—the melt rheology under actual processing conditions—to permit evaluation of at least the order of magnitude of the other contributing factors mentioned above.

Melt rheology has been estimated in past work[2] from knowledge of the resin moelcular weight (usually expressed as inherent viscosity, *I.V.*) or from measurements using extrusion or rotational viscometers. But, in the latter case, instrument limitations made it necessary to extrapolate from model compounds which were too highly plasticized, tested at temperatures higher than the actual processing temperature, or at shear rates higher than those actually involved in foaming, namely, 1.0 sec^{-1} or less. Further, it has not heretofore been possible to separate the viscous and elastic components of melt flow and determine their relative contribution to processability.

The Rheometrics Mechanical Spectrometer (Rheometrics, Inc., 13 Beverly Drive, Belle Meade, New Jersey 08502; or I. Mass, Box 134, Accord (Hingham), Mass. 02018) is capable of separating elastic modulus and viscosity and of measuring actual plastisol melts at compositions, temperatures, and shear rates approximating those used in commercial processing. In the present work, the choice of material variables was limited to emphasize changes in rheology and maintain the other contributing factors such as surface activity as nearly constant as possible. For example, the PVC resins chosen were pre-

TABLE I
Compositions of Samples in Set A[a]

Plasticizer		Sample number		
Type	Level, phr	*I.V.* = 0.88	*I.V.* = 0.95	*I.V.* = 1.20
DOP/BBP (1/1)	60	1	5	—
DOP/BBP (1/1)	90	2	6	—
DOP	60	3	7	—
DOP	90	4	—	8

[a] All recipes contain 3 phr dibutyltin bisisooctyl thioglycollate.

pared under similar conditions and vary primarily in molecular weight,[3] and the plasticizer type was limited to di-2-ethylhexyl phthalate (DOP) for the most part with some tests made with DOP–butylbenzyl phthalate (BBP) blends.

The melt viscosity of these simple systems was found to correlate usefully with foam processability. The elastic modulus results could not be as readily related to foaming, and this is discussed later in terms of the effects of particulate and microcrystalline structure.

EXPERIMENTAL

Instrument and Operating Conditions

The Rheometrics Mechanical Spectrometer was used with a parallel-plate assembly operated in the orthogonal mode, Figure 1. The symbols, with dimensions and units, are as follows: R = radius of the plate, 2.5 cm; a = eccentricity, 0.05 or 0.10 in.; h = gap, 0.01 or 0.02 in.; γ = strain, a/h, 5; F_x and F_y = forces in x and y direction, gram forces, simultaneously recorded on the chart; G' = elastic modulus, dynes/cm^2; $G' = 50 F_y (h/a) = 10 F_y (h/a$ was maintained constant at .005/.001 or .010/.002); G'' = loss (viscous) modulus; and $G'' = 50 F_x (h/a) = 10 F_x$. The normal force F_z measurements were not performed.

The frequency of operation was 1.0 rad/sec, but 0.1 rad/sec was also used for selected samples. The temperature of measurements were 175° and 195°C.

Samples

Two sets of samples were used: the compositions of samples in set A are given in Table I and those of set B, in Table II.

With set A samples, films 0.025–0.030 in. thick were cast from the plastisols and heated for 3 min in an air oven set at 185°C to effect gelation and fusion. The rheological measurements of this set of samples were made at 195°C and 1 rad/sec with the platen gap preset at 0.020 in.

The samples of set B were cast into thicknesses of 0.012–0.015 in. heated

TABLE II
Compositions of Samples in Set B[a]

Plasticizer		Sample number		
Type	Level, phr	I.V. = 0.88	I.V. = 1.03	I.V. = 1.20
DOP	50	9	—	—
DOP	75	10	—	—
DOP	95	—	—	13
DOP	100	—	12	—
DOP	120	11	—	14
DOP	150	—	—	15

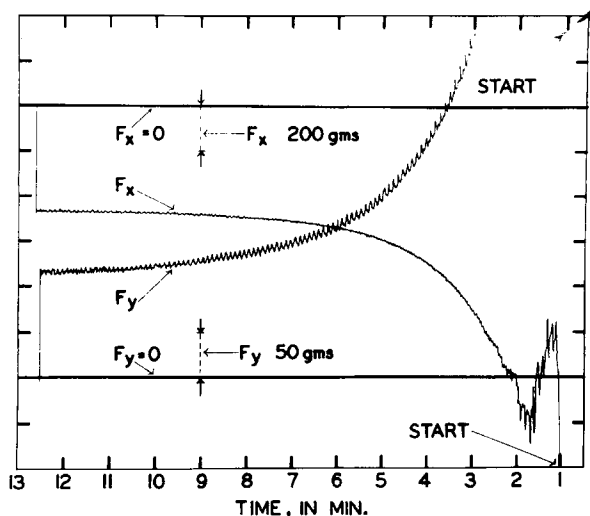[a] All recipes contain 5 phr dibasic lead phthalate added as an ink-milled dispersion in DOP.

Fig. 2. Recording of forces in spectrometer (typical).

for 5 min in an air oven set at 150°C to effect gelation. The rheological measurements were made at 175° and 195°C, both at 1 rad/sec with the platen gap preset at 0.010 in. With samples 10, 12, and 14, the measurements were made at 0.1 rad/sec and at a temperature of 175° and 195°C.

RESULTS

Figure 2 is a typical recording of forces F_x and F_y at 1 rad/sec. For the samples of set A, the forces were very high until the temperature equilibrated and the stress caused by closing the platen to the preset gap relaxed. With typical runs in set A, the forces became nearly constant after 8 min. Compositions with low plasticizer levels continued to decrease in force very slowly, and data were taken for calculation of G' and G'' at 10–15 min, close to steady state. Compositions with high plasticizer levels tended to reach minima in F_x and F_y at about 8 min and increased very slowly thereafter. In this case, G' and G'' were calculated from the minimum forces. This tendency for the forces to increase was attributed to plasticizer evaporation rather than thermal degradation of the compound because it occurred only in the more highly plasticized compounds and because inspection of the samples after comple-

TABLE III
Viscoelastic Data of Plastisols, Samples in Set A, at 195°C with 1.0 rad/sec

Sample no.	I. V.	Plasticizer level	$G' \times 10^{-3}$, dynes/cm^2	$G'' \times 10^{-3}$, dynes/cm^2
1	0.88	DOP/BBP 60	1.23 ± 0.07	5.1 ± 0.4
2	0.88	DOP/BBP 90	0.36 ± 0.02	1.33 ± 0.0
3	0.88	DOP 60	1.50	5.7
4	0.88	DOP 90	0.405 ± 0.005	0.865 ± 0.065
5	0.95	DOP/BBP 60	1.52	7.40
6	0.95	DOP/BBP 90	0.420 ± 0.02	1.82 ± 0.02
7	0.95	DOP 60	2.60	6.50
8	1.20	DOP 90	1.95 ± 0.05	5.95 ± 0.15

tion of the run (up to 15 min) showed only a very faint yellowish discoloration.

With samples in set B, the specimens used were thinner and were preheated for 4 min with the platens just contacting the specimen. After preheating, the upper platen was closed to the present gap. In this case, the forces reached an almost steady value 5 min after starting the machine. The readings were taken after 10 min.

The results of the calculation for 1 rad/sec runs were summarized in Table III for set A and Table IV for set B. Samples 1, 2, 4, and 8 were run in duplicate, and sample 6 was run in triplicate. Average values are shown with the extremes reported as the deviations. All other samples were run only once.

At 0.1 rad/sec, the forces, while roughly of the same magnitude as those at 1 rad/sec, oscillated slowly over a much wider range with somewhat irregular amplitude but a fairly regular period. An average curve was drawn on the recorder chart to estimate the trend of the forces over the 15-min test time. As at 1 rad/sec, the loss modulus leveled out to a practically steady value within 5 min. Unlike the results at the higher shear rate, the elastic modulus decreased continually. These data are presented in Table V.

Data Correlation

Plotted in Figure 3 are all the observed data of dynamic viscosity at 195°C and 1 rad/sec expressed as a function of polymer concentration in DOP. The

TABLE IV
Viscoelastic Data of Plastisols, Samples in Set B, at 175 ° and 195°C with 1.0 rad/sec

Sample no.	I.V.	DOP level	175°C		195°C	
			$G' \times 10^{-3}$	$G'' \times 10^{-3}$	$G' \times 10^{-3}$	$G'' \times 10^{-3}$
9	0.88	50	17.5	31.5	6.3	8.9
10	0.88	95	6.0	10	3.0	3.55
11	0.88	120	3.95	2.65	1.0	0.68
12	1.03	100	7.7	7.5	3.4	2.8
13	1.20	95	12.8	17.5	5.4	6.6
14	1.20	120	8.8	8.8	3.0	3.6
15	1.20	150	5.5	4.6	2.0	1.22

TABLE V
Viscoelastic Data of Plastisols at 175 and 195° C with 0.1 rad/sec

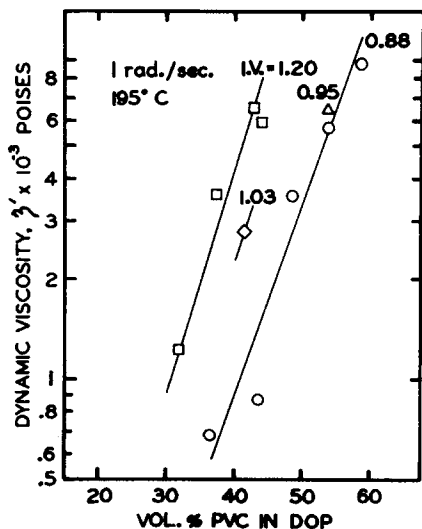| Sample no.	I.V.	DOP level	Elastic modulus $G' \times 10^{-3}$			Loss modulus $G'' \times 10^{-3}$		
			5 min	10 min	15 min	5 min	10 min	15 min
				175°C				
10	0.88	75	5.9	4.6	3.9	11.0	10.4	9.7
12	1.03	100	5.0	3.3	2.5	9.8	8.9	8.3
14	1.20	120	3.2	1.5	1.2	8.2	7.6	7.2
				195°C				
10	0.88	75	0.96	0.60	0.40	2.1	2.0	2.1
12	1.03	100	0.62	0.25	0.14	1.95	1.90	1.90
14	1.20	120	1.75	0.95	0.85	2.5	2.75	2.9

Fig. 3. Effect of polymer concentration in plasticized stock on observed dynamic viscosity (195°C).

lines are drawn through the points for an $I.V.$ = 1.20 and 0.88, respectively.

By using these lines, the relationships of Figure 4 were constructed. For a given $I.V.$ of the PVC resin, a required DOP level may be found from this figure to achieve a desired viscosity at 195°C and 1 rad/sec. The area enclosed by the broken lines is where the observed data are presently available. If the relationship is used further away from the area, the prediction may not be very accurate. However, the correlation was found to be useful down to an $I.V.$ = 0.68 to predict the product performance. The example was to reproduce the same quality of a foam originally made from an $I.V.$ = 0.76 resin with 70 phr DOP, marked (O) in Figure 4. Substitutions of the resin with other resins having $I.V.$ = 0.68, 0.78, and 0.94 were attempted. From Figure 4, the required DOP levels to maintain constant η' were found to be 60, 74, and 100 phr, respectively, marked (□) on the figure. The foams prepared from the predicted compositions were of the same quality. Moreover, with resin of an $I.V.$ = .94 and DOP levels of 80 and 90 phr, the forms were obviously different from the control.

Shown in Figure 5 is a relationship between dynamic viscosity at 195°C, 1 rad/sec, and molecular weight of resins expressed as $I.V.$, given for different DOP levels. The relationship was constructed from Figure 4, and all the observed points are shown in the figure. The accuracy of the graphs away from the observed ranges is not necessarily good.

The strong dependence of η' on molecular weight may be surprising. The data can be expressed according to

$$\eta' = K(I.V.)^n \tag{1}$$

where n varies from 3.6 at the lower dynamic viscosity to 6.9 at the higher viscosity.

Equation (1) can be separated into two parts:

$$\eta' = kM_w^p \tag{2}$$

and
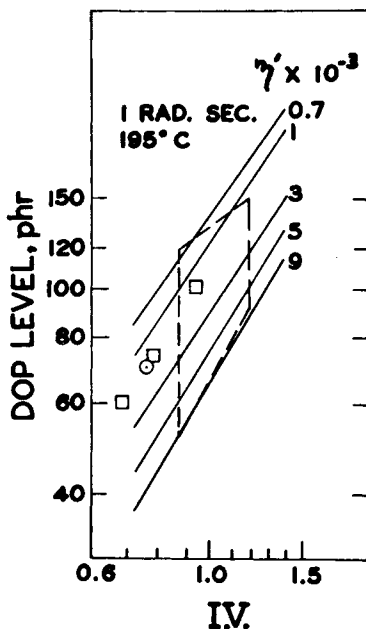
Fig. 4. Effect of DOP level and *I.V.* on dynamic viscosity.

$$I.V. = k'M_w^\alpha \tag{3}$$

Consequently,

$$\eta' = k(1/k')^{p/\alpha}(I.V.)^{p/\alpha} \tag{4}$$

$$n = p/\alpha. \tag{5}$$

The value of p has been shown to be approximately 3.4 for many polymer melts when η' is measured under Newtonian flow conditions. Comparison of data at 0.1 and 1.0 rad/sec shows that the material behavior is far from Newtonian (Fig. 10). In general for non-Newtonian systems, p is dependent on shear rate and is less than 3.4, probably nearer to 2 or 3. The value of α has been recently determined[5] to be 0.59 when *I.V.*, as here, is determined with 0.2 g/100 ml cyclohexanone solution at 30°C. Thus, for n in the range of 3.6 to 6.9, p can be calculated, and it ranges from 2.1 to 4.1; the lower value is in the expected range. The higher value of p is larger than the previously mentioned value of 3.4, observed with amorphous polymer melts. The reason for the sensitive dependence of η' on *I.V.* (molecular weight) is not known yet and requires further study.

Processing experience with vinyl foam has shown considerable effect from substitution of highly solvating plasticizers for DOP in many formulations. Table VI summarizes some direct comparisons of storage modulus and dynamic viscosity of model recipes where this was done. The data were taken at 195°C and 1.0 rad/sec.

Under the test conditions, there was no clearly systematic effect on rheology. This leads to the tentative conclusion that the influence of highly solvating materials is via their effect on melt rheology as the vinyl stock is being heated through the initial lower temperature stages of blow, but confirmation
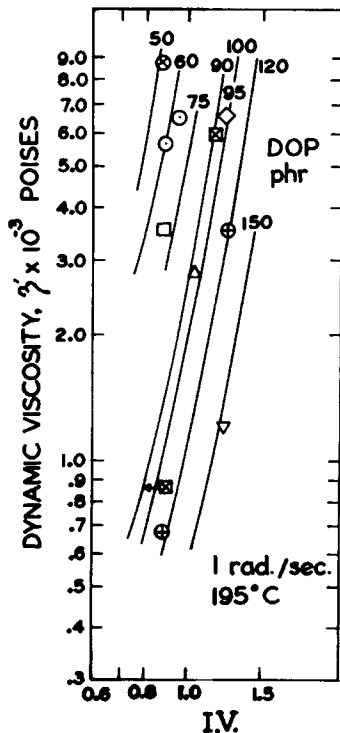
Fig. 5. Dynamic viscosity as a function of inherent viscosity of resin and level of plasticizer in stock.

will have to await measurements of melt rheology at lower temperature and shear rate as a function of plasticizer choice.

The data obtained at 175°C are shown in Figure 6 where η' is plotted against the volume per cent of PVC. Less data were available, but this figure shows the effect of plasticizer concentration on viscosity to be roughly the same on a percentage basis at 175°C as at 195°C. (Compare slopes in Figs. 3 and 6.) Assuming the validity of an Arrhenius relationship, the viscosity–temperature behavior for any given plasticizer level can be plotted from the data of Figures 3 and 6. Figure 7 is such a plot for 58.8 vol-% PVC (95 phr DOP) and 37.3 vol-% PVC (120 phr DOP). Data of the sort in Figure 7 should permit rapid estimation of the modification required in processing temperature to maintain good-quality foam in the face of desired changes in plasticizer level.

The storage moduli observed at 195°C are plotted in Figure 8 for all DOP

TABLE VI
Viscoelastic Data—Comparison of DOP with DOP/BBP

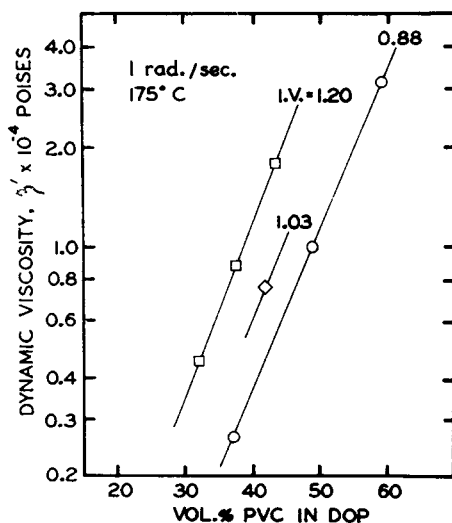| I. V.	0.88	0.88	0.88	0.88	0.95	0.95
Plasticizer, phr	60	60	90	90	60	60
Plasticizer type	DOP	DOP/BBP	DOP	DOP/BBP	DOP	DOP/BBP
$G' \times 10^{-3}$ dynes/cm^2	1.50	1.23 ± 0.07	0.405 ± 0.005	0.36 ± 0.02	2.60	1.50
$\eta' \times 10^{-3}$, poises	5.7	5.1 ± 0.4	0.865 ± 0.065	1.33 ± 6.0	6.50	7.40

Fig. 6. Effect of polymer concentration in plasticized stock on observed dynamic viscosity (175°C).
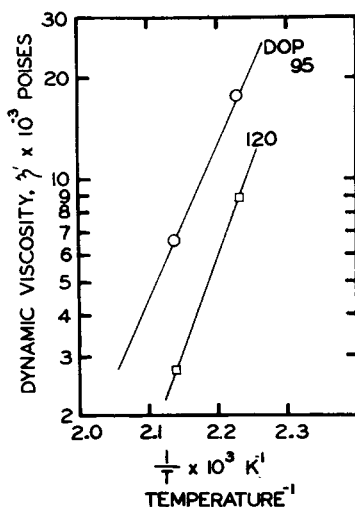

Fig. 7. Dynamic viscosity–temperature behavior at 95 and 120 phr DOP from data in Figs. 3 and 6 for *I.V.* = 1.2.

systems. The moduli of set A samples are consistently lower than those of set B samples. The elastic modulus may be more sensitive to the presence of gel structure in that the difference in the gelation (and fusion) temperature for the sample preparation may be responsible for the disagreement. Namely, set A samples had been treated in an oven at 185°C for 3 min, and set B samples had been heated at 150°C for 5 min. The set A samples are more effectively fused and, therefore, they have much less gel structure than the set B samples. If this interpretation is correct, the measurement of elasticity can be used as a very effective measure of gel structure remaining in incompletely fused materials. Another possibility is the differences in preheating time and sample handling procedures. These points require further study.
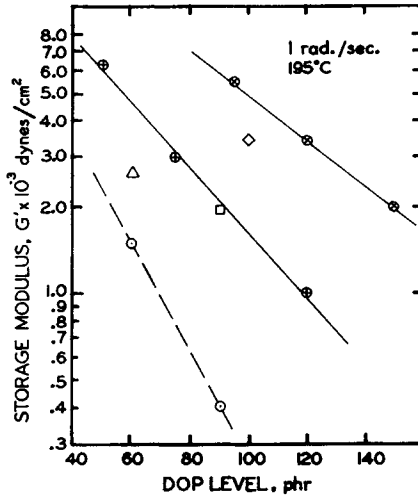
I.V.	Set A	Set B
0.88	(⊙)	(⊕)
0.95	(△)	
1.03		(◇)
1.20	(□)	(⊕)

Fig. 8. Storage modulus vs. effect of DOP level, *I.V.*, and processing conditions:
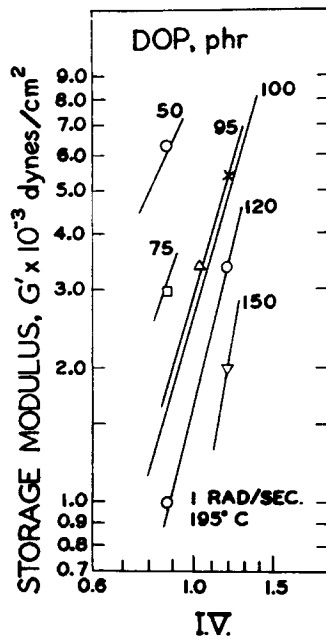

Fig. 9. Storage modulus as a function of inherent viscosity and level of plasticizer in stock (set B only).
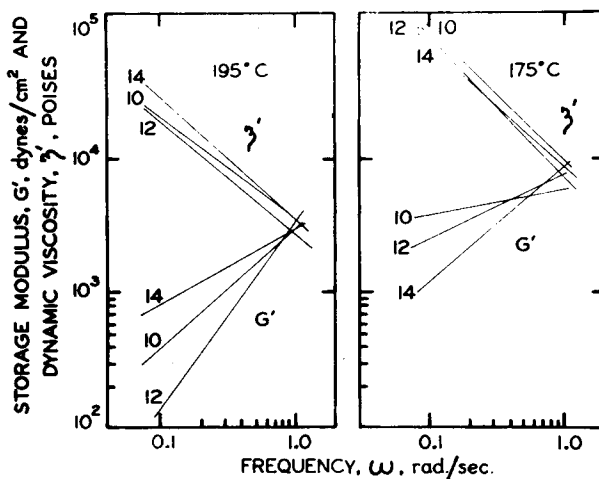
Fig. 10. Effect of frequency ("shear rate") on melt rheology.

The data of set B at 195°C are replotted in Figure 9 to show the dependence of G' on $I.V.$ at different DOP levels. Comparison with Figure 5 indicates roughly the same trend for G' and η' as $I.V.$ and plasticizer level change. But, as mentioned, G' seems to be affected by processing and by plasticizer choice.

Shown in Figure 10 are the frequency dependences of storage modulus and dynamic viscosity at 175° and 195°C. Three samples having similar viscosity were selected from set B samples. Although the precision of the data has not been evaluated yet, the following comments may be made. First of all, the viscosity is not independent of frequency, i.e., there is non-Newtonian behavior even at these low frequencies. Very high dependence of viscosity on frequency implies that the system has structure. Of course, presence of particulate and microcrystalline structures has been known[5-9] in PVC. Secondly, the storage moduli show far more variations, even though the viscosities are similar. Again, this may be interpreted that elasticity is affected more by the presence of structure and that these three samples have different degrees of structure. Such structural difference may be inherited from differences in the original resin, surface characteristics, or other factors.

CONCLUSIONS

It was shown that the low shear viscosity, i.e., 0.1–1.0 rad/sec, may be effectively used for formulating PVC plastisol for foam application. Viscosities are measured in the temperature range corresponding to foam preparation. The material variables correlated are the resin molecular weight expressed as $I.V.$ and the plasticizer type and level.

The observation of storage modulus seems to indicate that the elasticity is much more sensitively affected by the structure present in the system. Such structure is inherent in PVC systems and known to be particulate and microcrystalline in origin. The progress of fusion reduces some of these structures, particularly the ones originated from the resin powder. The decrease of storage modulus upon continuing heat treatment seems to indicate the reduction

of such structure.   Furthermore, it may be speculated that the stability of the foam upon prolonged heating and/or overheating may be related to the structural change, which may be characterized by the change of elasticity.

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