

Terpolymers. III. Isochronal Viscoelastic Parameters for Terpolymers of Vinyl Stearate, Vinyl Acetate, and Vinyl Chloride

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Synopsis

Isochronal viscoelastic parameters were collected for many of the copolymers, terpolymers, and diluent mixtures whose mechanical properties at ambient temperatures were reported in the preceding paper. In the polymeric systems, vinyl stearate, acting as the primary internal plasticizer, was introduced into terpolymers by displacing vinyl acetate from base copolymers of vinyl acetate and vinyl chloride, across the range of composition. In the diluent mixtures, poly(vinyl chloride) was plasticized by di-2-ethylhexyl phthalate across the range of compositions. For direct comparison with the mixtures, vinyl chloride was plasticized by copolymerization with vinyl stearate across the same range of compositions. Moduli for the co- and terpolymers reached the low values characteristic of soft materials at room temperature only through a short range of vinyl stearate composition. At higher internal plasticizer compositions, side-chain crystallization stiffened the samples and raised their moduli. In contrast, moduli for the mixtures decreased steadily with increase in diluent at ambient temperature. The effective use temperature ranges were narrow for the co- and terpolymers but broad for the mixtures. Curve broadening was similar for both types of systems, but reached a maximum at about 40 weight-% plasticizer for the diluent mixtures. The slopes of the glassy modulus with decreasing temperature at 50°C below T_g for the vinyl stearate copolymers were relatively large. However, moduli close to that of poly(vinyl chloride) were reached only near the temperature range associated with the γ -transition. Consequently, this behavior was attributed to motions of the side chains in the glassy matrix. Room temperature moduli, which could be obtained before the onset of melting, were correlated with the fractional side-chain crystallinity for polymers having a high vinyl stearate content. From this relation, the modulus for the hexagonal crystal form of the side-chain crystallites of poly(vinyl stearate) was estimated to be 1.2×10^{10} dynes/cm². Moduli for the glassy amorphous phase of this same polymer appeared to have one sixth of this value at 40°C below the glass transition. The glass transition temperature occurred about 10° below the inflection temperature at 10^9 dynes/cm², as an average for all of the systems studied.

INTRODUCTION

In the preceding paper,¹ glass transition and mechanical data were obtained for copolymers of vinyl stearate and vinyl chloride, and for ter-

polymers incorporating these two comonomers and vinyl acetate, over all compositions. Correlations were made against the weight fraction of vinyl stearate, which acted as the primary plasticizer. Comparisons were also made with data for poly(vinyl chloride) externally plasticized with di-2-ethylhexyl phthalate (DOP). Thus, in the previous paper, modulus-composition data at ambient temperatures were emphasized. In this paper, isochronal modulus-temperature data are presented for these same systems. A prime purpose of this study is to present viscoelastic parameters in a form permitting direct comparison with similar quantities in the literature for poly(vinyl chloride) externally plasticized by a variety of plasticizers.²⁻⁵ Comparisons with amorphous homopolymers similarly plasticized⁶ will also be permitted.

In this way, it was felt that the major differences in properties conferred by external and internal plasticization of poly(vinyl chloride) and selected amorphous homopolymers would be sharply delineated. To this end, moduli are given here in dynes/cm² instead of in lb/in.², as in the previous paper.¹ Additionally, the superior properties uniquely conferred on externally plasticized poly(vinyl chloride) by residual main-chain crystallinity^{2,7-11} could be contrasted with the properties of the copolymers and terpolymers, where this crystallinity was presumably eliminated.¹² Crystallinity in poly(vinyl chloride) acts to raise and support the moduli in the rubbery region of mechanical response³⁻⁵ and thereby to greatly extend the temperature range of useful properties. This behavior is absent in plasticized amorphous homopolymers⁶ unless, as in certain block copolymers, small glassy inclusions can act as tie points in a rubbery matrix¹³ and thereby raise and support moduli in a controlled fashion. In analogy with this principle, special attention will be given to the correlation of modulus with side-chain crystallinity,¹⁴⁻¹⁸ which developed in these copolymers and terpolymers beyond a critical weight fraction of vinyl stearate.

EXPERIMENTAL

Experimental procedures were given in the preceding paper.¹ The Clash-Berg apparatus¹⁹ was used, without concomitant use of the Gehman apparatus,²⁰ to determine moduli in this study. Consequently moduli below about 3.5×10^7 dynes/cm² were considered to be less accurate because of the insensitivity of the instrument in this region. Moduli reported below this value are considered to be only qualitatively indicative of soft materials. Moduli are reported as three times the shear moduli G , on the assumption that Young's modulus $E \sim 3G$.^{3,11} A deformation frequency of 5 sec was used in this work. This is close enough³¹ to frequencies of 10 sec usually reported in the literature^{3-5,10} to permit direct comparison. The procedure used followed ASTM Standards D1043-61T. Notations of the previous work¹ were followed here with respect to weight w_i and mole fraction m_i in the equations and figures. Lettered subscripts are

assigned as follows: VS, vinyl stearate; VA, vinyl acetate; VCL, vinyl chloride.

Some of the heats of fusion used to calculate fraction crystallinity in this paper are listed in Table II of the previous paper.¹ The rest are: experiment number (underlined), ΔH_f (cal/g): 21a, 0.505; 26a, 2.47; 26b, 4.47; 36a, 0.948; 36b, 2.15; 36c, 3.35; 36d, 6.84; 36e, 9.00; 43a, 0.688; 43b, 4.20; 43c, 6.53; 43d, 8.24; 52a, 0.325; 52b, 0.524; 52c, 0.960; 52d, 4.35; 52e, 7.18.

RESULTS AND DISCUSSION

General Features

All of the viscoelastic parameters are listed in Table I. The experimental numbers correspond to those listed in Tables I and II of the preceding paper. This arrangement permits ready comparison of the two sets of data. Those bearing subscripts lettered in lower case in this paper were mentioned in footnotes of corresponding tables in the preceding paper. These are the terpolymers displaying significant side-chain crystallinity. Some of their heats of fusion are given in the experimental sections. The terpolymers in Table I of this paper are separated into sets according to their vinyl chloride mole fraction content. Experiments 16, 19, 22, 27, 37, and 44 are the base copolymers of vinyl acetate and vinyl chloride; the balance are terpolymers wherein the initial mole fraction of vinyl acetate is successively replaced by vinyl stearate in each set. The first set in the table (experiments 1-13) are copolymers of vinyl stearate and vinyl chloride. The last set are mixtures of di-2-ethylhexyl phthalate (DOP) and poly(vinyl chloride). Glass transition temperatures are those reported in the previous paper.¹

The designations for the viscoelastic parameters in Table I follow those used by Tobolsky³⁻⁵ and Iobst¹¹ and co-workers, but with some modifications. These parameters may be better seen by reference to the zones indicated by slash marks in the curves in Figures 1 and 2. The approximate inflection temperature T_i was taken as the modulus at 10^9 dynes/cm², while s is the slope at T_i . The moduli $3G_1$ and $3G_2$ were taken at 50°C below and 50°C above T_1 , respectively.⁴ Because the moduli at $3G_2$ were generally too low for the sensitivity of the instrument, the few listed in the table are only approximate; those obtained by a short extrapolation are even rougher approximations and serve only to indicate trends. Of greater significance is the temperature at which the modulus reached 3.45×10^7 dynes/cm² ($T_{3.45}$) (as marked by the lowest slashes in Figs. 1 and 2). This value was chosen as a modulus characteristic of a softly plasticized material. The difference between this temperature and T_i (ΔT) in the Table, then, indicates the upper use temperature range, especially when considered in conjunction with the slope at $T_{3.45}$. This is designated s_2 in the table. If s_2 is large and ΔT small, the modulus is changing rapidly through a narrow

TABLE I
Glass Transition Temperatures and Viscoelastic Parameters from Modulus-Temperature Curves

| Experiment no. ^a | w_{VS} | T_g , °C | T_i , °C | $-s$ | $3G_1$, dynes/cm ² × 10 ⁻¹⁰ | $-s_1$ | $3G_2$, dynes/cm ² × 10 ⁻⁷ | $T_{3.45^b}$ | $-s_2^c$ | ΔT , °Cd |
|---|----------|------------|------------|-------|--|--------|---|--------------|----------|------------------|
| Copolymers: Vinyl Stearate and Vinyl Chloride | | | | | | | | | | |
| 1 | 0 | 80.9 | 89.5 | 0.14 | 2.4 | 0.0017 | 6.0 | 174.0 | 0.0041 | 84.5 |
| 2 | 0.113 | 58.9 | 66.4 | 0.084 | 2.5 | 0.0024 | 3.2 | 110.0 | 0.0054 | 43.6 |
| 3 | 0.207 | 40.9 | 50.0 | 0.12 | 2.0 | 0.013 | 2.6 | 74.0 | 0.011 | 24.0 |
| 4 | 0.287 | 24.9 | 40.0 | 0.12 | 1.7 | 0.0039 | 1.3 ^e | 54.0 | 0.025 | 14.0 |
| 5 | 0.356 | 12.9 | 26.2 | 0.086 | 1.3 | 0.0051 | 1.9 ^e | 43.5 | 0.025 | 17.3 |
| 6 | 0.415 | 0.9 | 16.5 | 0.069 | 1.2 | 0.0054 | 1.5 ^e | 36.0 | 0.024 | 19.5 |
| 7 | 0.467 | 1.9 | 9.7 | 0.053 | 1.0 | 0.0011 | 0.83 ^e | 27.5 | 0.041 | 17.8 |
| 8 | 0.513 | 7.9 | 13.0 | 0.073 | 1.2 | 0.0074 | 0.67 ^e | 36.3 | 0.040 | 23.3 |
| 9 | 0.554 | 16.9 | 13.5 | 0.056 | 1.1 | 0.0077 | 0.48 ^e | 39.0 | 0.044 | 25.5 |
| 10 | 0.624 | 18.9 | 30.0 | 0.027 | 0.76 | 0.0089 | | 40.0 | 2.0 | 10.0 |
| 11 | 0.641 | 18.9 | 35.5 | 0.038 | 0.76 | 0.0075 | | 40.0 | 2.8 | 4.5 |
| 12 | 0.768 | 6.9 | 39.0 | 0.094 | 0.59 | 0.0061 | | 45.0 | 1.0 | 6.0 |
| 13 | 0.833 | 6.9 | 43.0 | 0.29 | 0.50 | 0.055 | | 45.0 | 5.0 | 2.0 |
| Terpolymers: Vinyl Chloride, Mole Fraction 0.85 | | | | | | | | | | |
| 16 | 0 | 62.9 | 55.5 | 0.12 | 2.6 | 0.0024 | 2.3 | 74.0 | 0.018 | 18.5 |
| 17 | 0.201 | 26.9 | 43.3 | 0.25 | 2.3 | 0.0020 | 2.6 ^e | 54.5 | 0.018 | 11.2 |
| 18 | 0.351 | 13.9 | 25.0 | 0.075 | 1.1 | 0.0048 | 1.2 ^e | 38.0 | 0.076 | 13.0 |
| Terpolymers: Vinyl Chloride, Mole Fraction 0.80 | | | | | | | | | | |
| 19 | 0 | 66.9 | 47.0 | 0.27 | 2.3 | ≈ 0 | 2.4 ^e | 64.0 | 0.11 | 17.0 |
| 20 | 0.198 | 33.9 | 39.7 | 0.10 | 1.9 | 0.0013 | 2.2 ^e | 55.0 | 0.029 | 15.3 |
| 21 | 0.346 | 8.9 | 24.0 | 0.20 | 1.1 | 0.0063 | | 37.5 | 0.052 | 13.5 |
| 21a | 0.462 | 1.9 | 14.0 | 0.067 | 1.1 | 0.0083 | | 35.0 | 0.18 | 21.0 |

Terpolymers: Vinyl Chloride, Mole Fraction 0.75

| | | | | | | | | | | |
|-----|-------|------|------|-------|------|--------|------|------|-------|------|
| 22 | 0 | 62.9 | 66.5 | 0.20 | 2.9 | 0.0041 | 2.6° | 80.0 | ≈0 | 13.5 |
| 23 | 0.195 | 26.9 | 44.0 | 0.45 | 1.7 | ≈0 | 1.4° | 51.8 | 0.078 | 7.8 |
| 24 | 0.273 | 17.9 | 30.0 | 0.11 | 1.5 | 0.0040 | 1.9° | 41.5 | 0.059 | 11.5 |
| 25 | 0.342 | 7.9 | 22.3 | 0.083 | 1.2 | 0.0064 | 1.5° | 36.0 | 0.10 | 13.7 |
| 26 | 0.456 | 1.9 | 14.0 | 0.073 | 1.2 | 0.0083 | 1.4° | 31.0 | 0.054 | 17.0 |
| 26a | 0.548 | 20.9 | 14.0 | 0.060 | 1.0 | 0.0063 | | 35.0 | 1.13 | 21.0 |
| 26b | 0.588 | 21.9 | 27.0 | 0.039 | 0.81 | 0.0009 | | 40.0 | 0.097 | 13.0 |

Terpolymers: Vinyl Chloride, Mole Fraction 0.60

| | | | | | | | | | | |
|-----|-------|------|------|-------|------|--------|------|------|-------|------|
| 27 | 0 | 54.9 | 58.0 | 0.14 | 3.2 | ≈0 | 1.9° | 73.5 | 0.053 | 15.5 |
| 28 | 0.100 | 38.9 | 41.5 | 0.28 | 1.8 | ≈0 | 1.8° | 49.0 | 0.12 | 7.5 |
| 29 | 0.187 | 25.9 | 35.7 | 0.27 | 2.0 | ≈0 | | 46.0 | 0.037 | 10.3 |
| 32 | 0.262 | 13.9 | 24.0 | 0.14 | 1.5 | 0.0046 | | 38.0 | 0.051 | 14.0 |
| 35 | 0.329 | 2.9 | 15.5 | 0.14 | 1.4 | 0.0065 | | 33.0 | 0.070 | 17.5 |
| 36 | 0.388 | -5.1 | 14.0 | 0.092 | 1.3 | 0.0062 | 1.8° | 28.0 | 0.056 | 14.0 |
| 36a | 0.441 | 3.9 | 14.0 | 0.086 | 1.1 | 0.0072 | | 35.0 | 0.27 | 21.0 |
| 36b | 0.489 | 16.9 | 15.0 | 0.059 | 1.0 | 0.0070 | | 35.0 | 0.088 | 20.0 |
| 36c | 0.532 | 16.9 | 19.0 | 0.047 | 0.97 | 0.0062 | | 35.0 | 0.033 | 16.0 |
| 36d | 0.606 | 16.9 | 31.0 | 0.047 | 0.74 | 0.0080 | | 40.5 | 0.11 | 9.5 |
| 36e | 0.669 | 9.9 | 33.0 | 0.24 | 0.75 | 0.0089 | | 41.0 | 0.090 | 8.0 |

Terpolymers: Vinyl Chloride, Mole Fraction 0.40

| | | | | | | | | | | |
|-----|-------|------|------|-------|------|--------|-------|------|-------|------|
| 37 | 0 | 20.9 | 39.0 | 0.11 | 2.4 | ≈0 | 2.1° | 50.0 | 0.090 | 11.0 |
| 42 | 0.177 | 16.9 | 23.5 | 0.15 | 1.9 | 0.0035 | | 34.0 | 0.099 | 10.5 |
| 43 | 0.313 | -2.1 | 11.0 | 0.13 | 1.5 | 0.0083 | | 24.7 | 0.054 | 13.7 |
| 43a | 0.422 | 3.9 | 9.5 | 0.050 | 1.1 | 0.0065 | 0.69° | 30.0 | 0.051 | 20.5 |
| 43b | 0.511 | 8.9 | 20.5 | 0.048 | 1.0 | 0.0079 | | 35.0 | 0.11 | 14.5 |
| 43c | 0.585 | 21.9 | 29.7 | 0.066 | 0.90 | 0.0068 | | 44.0 | 0.017 | 14.3 |
| 43d | 0.647 | 11.9 | 34.0 | 0.13 | 0.76 | 0.0085 | | 40.0 | 0.17 | 6.0 |

TABLE I (continued)

| Experiment no. ^a | w_{VS} | T_g , °C | T_i , °C | $-s$ | $3G_1$, dynes/cm ² × 10 ⁻¹⁰ | $-s_1$ | $3G_2$, dynes/cm ² × 10 ⁻⁷ | $T_{3.45}^b$ | $-s_2^c$ | ΔT , °C ^d |
|--|----------|------------|------------|-------|--|--------|---|--------------|----------|------------------------------|
| Terpolymers: Vinyl Chloride, Mole Fraction 0.20 | | | | | | | | | | |
| 44 | 0 | 23.9 | 30.5 | 0.16 | 2.2 | ≈ 0 | 1.7 ^e | 40.0 | 0.055 | 9.5 |
| 52 | 0.168 | 11.9 | 26.0 | 0.20 | 1.3 | 0.0022 | | 36.0 | 0.099 | 10.0 |
| 52a | 0.299 | 11.9 | 14.0 | 0.11 | 1.4 | 0.0068 | | 24.0 | 0.11 | 10.0 |
| 52b | 0.355 | 9.9 | 8.5 | 0.083 | 1.2 | 0.0065 | | 22.0 | 0.062 | 13.5 |
| 52c | 0.405 | 6.9 | 11.0 | 0.088 | 1.4 | 0.0056 | | 29.0 | 0.023 | 18.0 |
| 52d | 0.492 | 21.9 | 19.0 | 0.049 | 1.1 | 0.0043 | | 36.0 | 0.11 | 17.0 |
| 52e | 0.565 | 16.9 | 29.0 | 0.060 | 0.97 | 0.0057 | | 40.0 | 0.21 | 11.0 |
| Mixtures: Di-2-ethylhexyl Phthalate (DOP) and Poly(vinyl Chloride) | | | | | | | | | | |
| 53 | 0.048 | 58.9 | 72.0 | 0.20 | 2.7 | 0.0007 | 4.8 | 134 | 0.0092 | 62.0 |
| 54 | 0.113 | 41.9 | 57.0 | 0.094 | 2.6 | 0.0009 | 4.2 | 128 | 0.0052 | 71.0 |
| 55 | 0.207 | 11.9 | 38.0 | 0.064 | 1.7 | 0.0065 | 3.1 | 80.0 | 0.0045 | 42.0 |
| 56 | 0.287 | -2.1 | 16.0 | 0.044 | 1.8 | 0.0067 | 3.5 | 66.0 | 0.010 | 50.0 |
| 57 | 0.356 | -21.0 | -3.0 | 0.046 | 2.3 | 0.012 | 4.4 | 57.0 | 0.016 | 60.0 |
| 58 | 0.415 | -41.1 | -17.0 | 0.050 | 2.6 | 0.0061 | 4.1 | 40.0 | 0.0075 | 57.0 |
| 59 | 0.467 | -45.1 | -28.3 | 0.065 | 2.6 | 0.0077 | 3.5 | 21.7 | 0.0063 | 50.0 |
| 60 | 0.554 | -53.1 | -43.0 | 0.078 | 2.1 | ≈ 0 | 3.5 | 7.0 | 0.0056 | 50.0 |
| 61 | 0.624 | -63.1 | -52.0 | 0.078 | 2.3 | ≈ 0 | 4.0 | -2.0 | ≈ 0 | 50.0 |

^a Experiment numbers correspond to the experiments listed in Tables I and II of the previous paper¹; the numbers with lettered subscripts are described in ref. 1 in the footnotes of Table I.

^b Temperature at which the modulus was 3.45×10^7 dynes/cm².

^c Slope at $T_{3.45}$.

^d $\Delta T = T_{3.45} - T_i$.

^e Estimated by a short extrapolation; data very approximate.

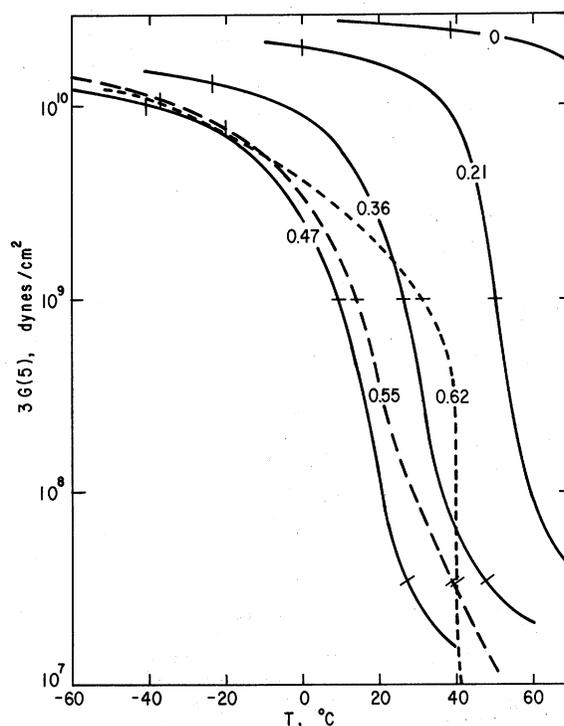


Fig. 1. Modulus-temperature curves for copolymers of vinyl stearate and vinyl chloride. Numbers indicate weight fraction of vinyl stearate. The corresponding mole fractions, in increasing order, are 0, 0.05, 0.10, 0.15, 0.20, 0.25. Slashes correspond to the designations $3G_1$, s , and s_2 of Table I, respectively. Solid lines are for amorphous copolymers; dashed lines are for copolymers exhibiting side-chain crystallinity. Measurements were at a frequency of 5 sec, as indicated in the ordinate.

temperature range close to the glass transition. On the other hand, if s_2 is close to zero and ΔT is large, the modulus is reaching a useful rubbery plateau at temperatures considerably above T_i . Consequently, the upper use temperature range is large. In similar fashion, a slope, s_1 , at $3G_1$ denotes the rate of change of modulus in the glassy region, 50°C below T_i . As can be seen from Table I, T_i lay 10 to 15°C above T_g in many cases. This relation will be discussed in greater detail in a later section. It can be seen that the moduli and slopes of Table I provide enough information to permit schematic isochronal curves to be constructed for all of the data collected.

The viscoelastic parameters of Table I showed relatively small differences between the various copolymers and terpolymers, but pronounced differences between these systems and the externally plasticized mixtures. The slope s decreased steadily for the copolymers and terpolymers but went through a minimum for the mixtures. The glassy slope s_1 , while variable, stayed in the range of 0.002 to 0.007 even for the mixtures. Exceptions were copolymers of vinyl acetate and vinyl chloride (the base copolymers)

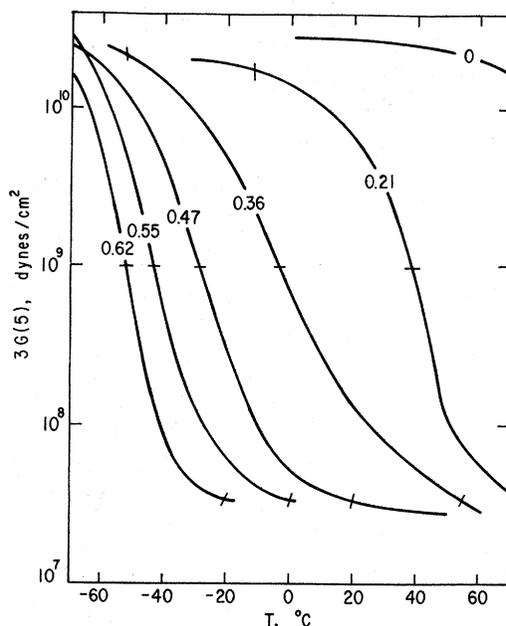


Fig. 2. Modulus-temperature curves for mixtures of di-2-ethylhexyl phthalate (DOP) and vinyl chloride. Numbers are weight fractions of DOP. Measurements were at a frequency of 5 sec, as indicated in the ordinate.

and those terpolymers rich in vinyl acetate. However, the glassy modulus, $3G_1$, decreased steadily for the copolymers and terpolymers, but not for the mixtures. A decrease in both $3G_1$ and s indicated a broadening of the isochronal curves coupled with a downward displacement on the vertical axis for the curves as vinyl stearate increased. The $3G_2$ values in Table I that were considerably below 3.45×10^7 dynes/cm², although insensitive, did indicate weak materials, of little utility at 50° above T_i . In contrast, the mixtures were entering their rubbery plateau, with moduli of 3.45×10^7 dynes/cm², in this temperature range. The more significant ΔT and s_2 values reflected this clearly. The difference ΔT was small and s_2 relatively large, being close to s , for the copolymers and terpolymers. On the other hand, ΔT was close to 50°C, or even greater, and s_2 was closer to zero for the diluent mixtures. Poly(vinyl chloride) plasticized with various external plasticizers^{2-6,11} exhibited such supported and extended rubbery regions, attributable to residual main-chain crystallinity.^{2,7-11} In contrast, when amorphous homopolymers were plasticized,^{3,6} their behavior more closely resembled that of the copolymers and terpolymers of this investigation. Thus, the polymerization process in the latter systems eliminates main-chain crystallinity.¹² The data for the copolymers and terpolymers further suggest that the molecular weight between entanglements has been extended to near the limit of the polymer molecular weight,²² so that viscous flow has become prematurely important. Any

observed decline in $D.P._n$ (Table I of the previous paper¹) with increasing vinyl stearate would further aggravate the effect.

These features may be more clearly seen from selected curves presented in Figures 1 and 2. Isochronal curves for copolymers of vinyl stearate and vinyl chloride at specific weight fractions (Fig. 1) contrast strikingly with the curves in Figure 2, where the same weight fraction of DOP was used as the diluent. The curves for the copolymers in Figure 1 were shifted to higher temperatures than those for the corresponding mixtures; the curves for the copolymers exhibiting side-chain crystallinity (dashed curves) were shifted more than those for the amorphous copolymers of lower ester content. The behavior of the amorphous copolymer systems reflected the lower efficiency of internal plasticizers in reducing T_g . This was discussed at length in the preceding paper¹ and in other recent papers.¹⁶⁻¹⁸ The crystalline system demonstrated the usual effect on properties conferred by high-modulus crystallites, dispersed throughout the polymer matrix. These can act as tie points for the amorphous chains, thereby restricting their motions. Thus, the development of side-chain crystallinity at a critical weight fraction of vinyl stearate ($\sim 0.4-0.5$) in simple co- and terpolymer systems militates against the possibility of attaining the same low-temperature flexibility as the external system by increasing the long-chain vinyl ester content. The contrast between the other viscoelastic features of the internally and externally plasticized systems (large s , s_2 , and small ΔT , decreasing $3G_1$, etc.), discussed at length in the above paragraphs, are obvious from the figures. Similar behavior was observed for the terpolymers. In the sections below, trends followed by the slope s and the glassy modulus $3G_1$, with vinyl stearate and DOP content, will be compared and briefly discussed. In a later section, the effect of side-chain crystallinity and the residual glassy amorphous regions on the modulus of poly(vinyl stearate) will be treated.

Relationship of $3G_1$ and s to Composition

Plots are shown in Figure 3 of the glassy modulus found 50°C below T_i ($3G_1$) in Table I against the weight fraction of vinyl stearate, w_{VS} , for all of the copolymers and terpolymers, as well as for the mixtures (w_{DOP}). The data followed the relation

$$3G_1 = 3G_{10} - kw_{VS} + k'(w_{VS})^2 \quad (1)$$

but k' was zero for the diluent system. These are the curves drawn through the data in the figure. They were computed using the constants in Table II, obtained by curve fitting with the computer. It is obvious that the moduli of the copolymers and terpolymers drifted to lower values, terminating in a computed value of 0.55×10^{10} dynes/cm² for vinyl stearate homopolymer. In contrast, the moduli for the mixtures were close to that of poly(vinyl chloride). When Clash-Berg curves for copolymers of both *n*-octadecyl and oleyl acrylate with methyl methacrylate¹⁷ were reexamined, somewhat similar moduli were found on extrapolation to a weight fraction

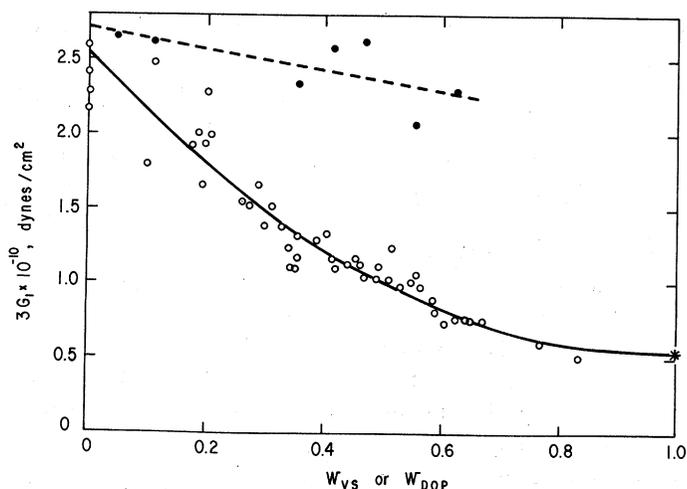


Fig. 3. Plot of $3G_1$ vs. weight fraction of vinyl stearate, w_{vs} , for copolymers and terpolymers in Table I (solid line) and weight fraction of di-2-ethylhexyl phthalate (DOP), w_{DOP} , (dashed line).

of unity, corresponding to the homopolymer. Poly(*n*-octadecyl acrylate) is crystalline¹, while the oleyl homopolymer was found to be amorphous.¹⁵ Consequently, the low glassy moduli seem to be characteristic of homopolymers having long side chains when examined considerably below T_g . It should be emphasized that $3G_1$ for the homopolymer and systems rich in vinyl stearate reflected contributions from both crystalline and glassy amorphous domains.¹⁴⁻¹⁶ On extrapolating the Clash-Berg curves for the copolymers of Figure 1 to the modulus found for poly(vinyl chloride) in Figure 3 (about 2.6×10^{10} dynes/cm²), the temperatures reached were approximately $-120^\circ \pm 15^\circ\text{C}$. This is in the vicinity of the γ -transition for certain polymers. This transition arises from motions in paraffinic chain segments greater than about four carbon atoms.²³⁻²⁵ It has recently been demonstrated^{1,17,18} that the presence of long side chains in comonomer units reduces the modulus of glassy systems in proportion to the free-

TABLE II
Parameters for the Various Equations

| Equation no. | Parameter | Copolymers and terpolymers | | Mixtures | |
|--------------|--------------|----------------------------|-------------|----------|-------------|
| 1 | $3G_{10}$ | 2.55 | ± 7.06 | 2.71 | ± 0.14 |
| | k | 4.15 | ± 0.42 | 0.704 | ± 0.34 |
| | k_1' | 2.15 | ± 0.56 | 0 | |
| 2 | s_0 | 0.163 | ± 0.006 | 0.203 | ± 0.016 |
| | A | 0.202 | ± 0.015 | 0.825 | ± 0.120 |
| | B | 0 | | 1.05 | ± 0.19 |
| 5 | $3G'_{(23)}$ | 17.88 | ± 0.15 | | |
| | α | 35.67 | ± 2.69 | | |
| | β | 67.18 | ± 8.89 | | |

volume contribution of each side-chain methylene group. The data of this paper suggest that the amplitude of the subgroup motions of the side chains in both crystalline and amorphous phases above the γ -transition is sufficient to reduce the solid-state modulus in the manner observed. This interpretation is, of course, highly speculative and receives little experimental support in view of the long extrapolation required from the limited data. It is intended as a stimulus to further investigation of the effect of subgroup motions on mechanical properties of systems modified by units containing long side branches.

The characteristic brittle failure of systems containing a high concentration of monomers having long side chains,^{17,18} including the systems of this paper, could arise around aggregates of the side chains and produce sufficient free volume to disturb the liquid structure. Clusters of crystalline side chains would behave as enhanced stress concentrators,²⁶ because the deformation energy would accumulate in imperfections along grain boundaries and in other crystal defects and give rise to the brittle fracture observed.^{1,17,18}

Values of the slopes s for the polymeric systems and mixtures were plotted against the weight fraction of plasticizer in Figure 4. Following curve fitting, the relation was

$$s = s_0 - A w_i + B (w_i)^2 \quad (2)$$

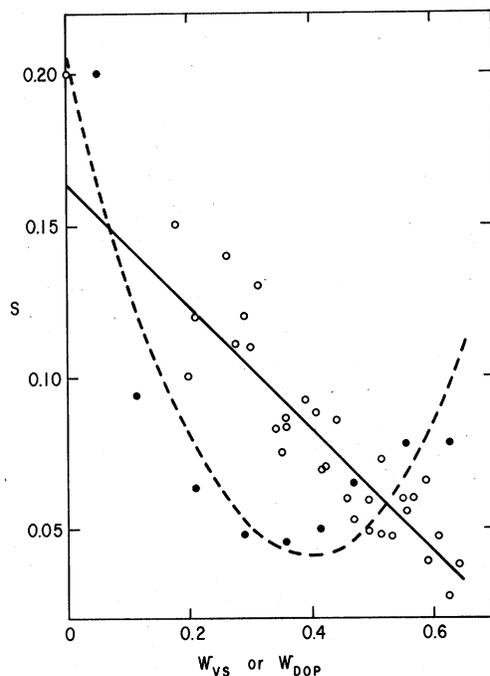


Fig. 4. Plot of s vs. weight fraction of vinyl stearate or di-2-ethylhexyl phthalate (DOP). Solid line and open circles, copolymers and terpolymers; dashed line and solid circles, mixtures.

where w_i is the weight fraction of either vinyl stearate or DOP and the other terms are constants. Their values are listed in Table II. The characteristic drift through a shallow minimum, found by Tobolsky⁵ for externally plasticized poly(vinyl chloride), is observed here. He attributed the minimum to contributions of both the polymer and plasticizer to the activation energy associated with the loss maximum in the intermediate plasticizer range. Solubility effects also influenced his data. Solubility between the side and main chain of the polymeric systems in this work is presumably absent, so that aggregation would characterize the mixing here. Aggregation can lead to curve broadening similar to that found for certain types of graft copolymers.^{27a} However, it is of some interest that the magnitude of the decline in s is similar for both types of systems.

Relationship Between Room Temperature Modulus and Side-Chain Crystallinity

Figure 1 demonstrated that moduli of copolymers of vinyl stearate and vinyl chloride were shifted up the temperature scale as side-chain crystallinity increased. A similar trend was also found for the glass transition temperature T_g and, of course, the inflection temperature T_i (Table I). In Figure 5, torsional moduli taken at room temperature, 23°C, for crystalline co- and terpolymers (Table I) were plotted as a function of fraction crystallinity associated with crystallizing methylene groups in the side chains, x_c . The crystallinity present in side chains may be computed¹⁵ using

$$x_c = (x_{c0}/\Delta H_{f0}) \Delta H_f \quad (3)$$

where the zero subscripts denote the crystallinity and heats of fusion, respectively, for the homopolymer.¹⁴ This equation follows because the crystallinity has been shown to be linearly related to the observed heat

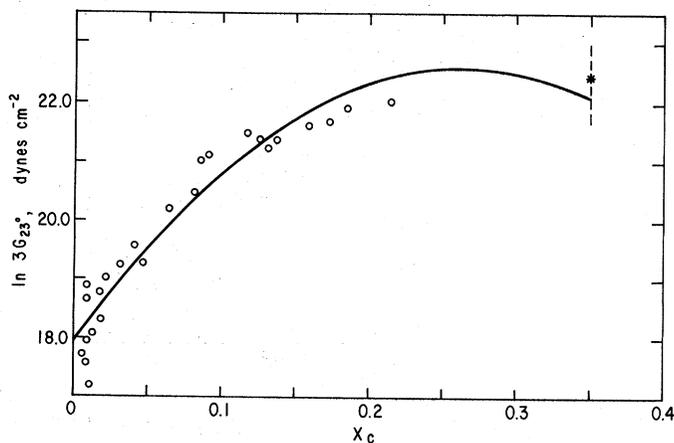


Fig. 5. Plot of room temperature moduli $3G_{23}$ vs. fraction of side-chain crystallinity x_c .

of fusion,¹⁴ which becomes a measure of that crystallinity. The fraction of amorphous polymer remaining, x_a , therefore is

$$x_a = (1 - x_c). \quad (4)$$

Moduli were taken at room temperature, because this temperature was generally below the onset of melting of even the small crystallites in these systems. Consequently, the rise in modulus is associated with effects contributed by the entirely crystalline solid phase. However, the moduli of the liquid phase coexisting with the solid phase presumably also rose, because the apparent T_g values of other copolymers were found to rise at high weight fractions of long side-chain comonomers.¹⁶ Since the apparent T_g of crystalline 18-carbon fatty vinyl esters is about 17°C,¹⁶ the T_g of the liquid phase in the present system always lay below room temperature. This temperature decreased as x_c decreased in the copolymers and terpolymers. Most of the rise in observed modulus, therefore, can be associated with hard crystal aggregates embedded in a softer amorphous matrix. The hard crystal nuclei concomitantly tie together amorphous chains and also gradually raise their moduli. As can be seen from Figure 5, the relation between modulus and the fraction crystallinity was

$$3G_{23} = 3G_{23}' e^{\alpha x_c - \beta x_c^2} \quad (5)$$

where $3G_{23}'$, α , and β are constants. Their values are presented in Table II. The solid lines drawn through the data points were obtained using eq. (5); the curve maximum between x_c of 0.22 to 0.32 is a trivial result of the statistical fit of the data. From eq. (5), the room temperature modulus of the homopolymer poly(vinyl stearate) may be estimated as 0.41×10^{10} dynes/cm². This value was obtained at the upper limit of the side-chain crystallinity content of the homopolymer, taken to be 0.35.¹⁴ This limit is shown as the dashed line in the figure. The star in the figure is the extrapolated value for the sum of the moduli of the glassy and crystalline regions of poly(vinyl stearate) from eq. (1), namely, 0.55×10^{10} dynes/cm².

If amorphous contributions to room temperature modulus are assumed to be negligible, the ratio of the estimated room temperature modulus to x_{c0} (0.41×10^{10} dynes cm²/0.35) will yield a crude estimate of the modulus of the entire hexagonal phase. The hexagonal crystal form has been shown¹⁴ to be the solid phase characteristic of both poly(vinyl stearate) and other homopolymers having long side branches. This computed modulus is 1.17×10^{10} dynes/cm². The assumption of low amorphous moduli has some factual justification. The glass transition temperature of the hypothetical amorphous poly(vinyl stearate), and other esters having 18-carbon side chains,¹⁶ were earlier estimated to be about -111°C. Materials having such low T_g values are well beyond the terminal region of the viscoelastic spectrum at room temperature and should therefore exhibit steady-flow viscosity. The fact that poly(vinyl stearate) and poly(*n*-octadecyl acrylate) are liquids of fairly low viscosity at a few degrees above their melting points suggests that the crystallites alone were stiffen-

ing the polymers of this investigation and making the major contribution to modulus. This conclusion has been reached by others.^{25,28} The estimated value of the modulus of the loosely packed hexagonal crystal modification of the side chains¹⁴ is not unreasonable. It is close to the modulus typical of glassy polymers. Moduli of this order were also found for the polyethylene crystal perpendicular to its chain axis²⁹ and for anthracene and acetanilide crystallizing in glassy styrene and acrylonitrile copolymer.³⁰ For example the modulus of the more densely packed orthorhombic polyethylene crystal is about 3×10^{10} dynes/cm².²⁹

The increased modulus resulting from embedding a hard filler in a polymer matrix was given by Nielsen^{27b} as

$$G = G_a v_a + A G_b v_b \quad (6)$$

where the subscripts a and b denote amorphous polymer and filler, respectively, and v_i is the volume fraction. The constant A is an adhesion parameter having limits of 0 to 1.0. If the crystallites in the homopolymer are considered to act as a hard filler, eq. (6) may be modified to yield the modulus of the glassy amorphous region in poly(vinyl stearate) at 50°C below T_i , as follows:

$$3G_{(a+b)} = 3G_a(1 - x_c) + 3G_b x_c \quad (7)$$

where $3G_{(a+b)}$ is the extrapolated modulus $3G_1$ for poly(vinyl stearate) of 0.55×10^{10} dynes/cm² from eq. (1), and $3G_b$ is the modulus of the crystal given above. The constant A is assumed to be unity because the amorphous methylene groups were also part of the crystallizing side chains. With these specifications, $3G_a$ was estimated by eq. (7) to be 0.22×10^{10} dynes/cm² at 50°C below T_i . As temperature was further decreased, $3G_{(a+b)}$ continually rose. Near the γ -transition, both $3G_a$ and $3G_b$ should have equalled 2.6×10^{10} dynes/cm², as discussed above. These calculations are, of course, very crude and speculative and need careful experimental verification. However, the computed values are of a reasonable magnitude and can serve to explain in part the phenomena observed. It is noteworthy that the effect of crystallinity on raising modulus is similar in magnitude to the increase conferred by crystallites in polyethylene and in other crystalline polymers.^{27c} However, extreme embrittlement remains a special characteristic for the fatty homopolymers.

Isochronal Temperature-Composition Diagram

Isochronal temperature-composition diagrams³¹ provide a useful method of expressing, in a simple way, the main trends of the data collected in this paper. These diagrams relate temperature and composition at fixed moduli, selected to demark the various regions of viscoelasticity in the polymers. Such diagrams are shown in Figure 6 for four systems selected as being representative of all of the data in Table I. Insert 1 illustrates the behavior of copolymers of vinyl stearate and vinyl chloride; insert 2

is that of the diluent mixture; and inserts 3 and 4 present data for the terpolymers containing 0.6 and 0.2 mole fraction of vinyl chloride, respectively. Readings taken vertically (isopleths) at constant composition are the isochronal temperature curves discussed throughout the paper. Readings taken horizontally at constant temperature (isotherms) parallel the moduli of the preceding paper in that moduli are a function of composition at constant temperature. Readings along each curve (isothernes) denote the change in temperature with composition at each viscoelastic level. Consequently, data in the area below the isotherne 10^{10} are for glassy polymers, and those considerably above $10^{7.54}$ are the terminal and steady-flow viscosity region. The data in the vicinity of the isothernes define the transition region and the onset of the rubbery plateau. The rubbery zone was not monitored in this work, but lay just above the isotherne $10^{7.54}$.

Comparison of inserts 1, 3, and 4 with insert 2 in Figure 6 shows clearly the main differences between external and internal plasticization of poly (vinyl chloride). If the isotherm 23°C is considered across the composition range, it is readily seen that the copolymers and terpolymers had only a small region where the isotherne 10^8 and $10^{7.54}$ lay close to the isotherm. These moduli denote soft polymers. Beyond that region, moduli rose as side-chain crystallinity commenced. The diluent mixtures, on the other hand, showed a large region of progressively softer composition as the plasticizer content increased. At very high DOP levels, true rubbery viscoelasticity was encountered at room temperature.² Additionally, the slopes of the isothernes at the right-hand side of inserts 1, 3, and 4 are less than for the mixtures (insert 2). This reflects the greater plasticizing efficiency of the diluent. The observation of the preceding paper¹ that low moduli were shifted to lower weight fractions of vinyl stearate as the vinyl acetate content of the base copolymer increased is confirmed by the details of the respective curves in inserts 1, 3, and 4. However, the initial moduli of the terpolymers had much less temperature dependence than was found for the copolymers of vinyl stearate and vinyl chloride (insert 1). This is also to be expected from the T_g behavior with composition (Table I and the preceding paper¹).

Consider, now, the isopleths at w_{VCL} (or $w_{\text{VA}} + \text{VCL}$) of 0.6 or 0.7. It may be seen that the moduli of the copolymers and terpolymers changed through a much narrower temperature range than did those of the diluent mixtures. Consequently, the use temperature range is much reduced for the copolymers and terpolymers. As was discussed extensively in a preceding section, the glassy isotherne moved to very low temperatures as the vinyl stearate content became large. This behavior was ascribed to the free volume contributed by movements of the side chains. The increased temperature dependence of the moduli, produced by side-chain crystallinity (seen in the curves at the left at a w_{VCL} of 0.3 to 0.5 in inserts 1, 3, and 4) and the narrow isothernic changes beyond 10^9 give a clear picture of the effect of the crystallites. Data in this composition range contrast markedly with data for the diluents (insert 2).

Thus, the curves in Figure 6, besides summarizing graphically the main points of the paper, also serve to indicate criteria important to the design of acceptable internal plasticizing systems through comparison with the desirable characteristics of the DOP mixtures. An acceptable system would afford high efficiency in reducing T_g , broad modulus-temperature curves, and a rubbery plateau of fairly high modulus ($3-5 \times 10^7$ dynes/cm²), maintained over a wide temperature range. Information is not given, however, on ultimate strength, which depends on relaxation processes occurring at extensions greater than those associated with linear viscoelasticity as studied in the present work.

Correlation of T_g and T_i

The relation between T_g and T_i was found from the data in Table I to follow the equation

$$T_g = T_i - (10.36 \pm 5.50). \quad (8)$$

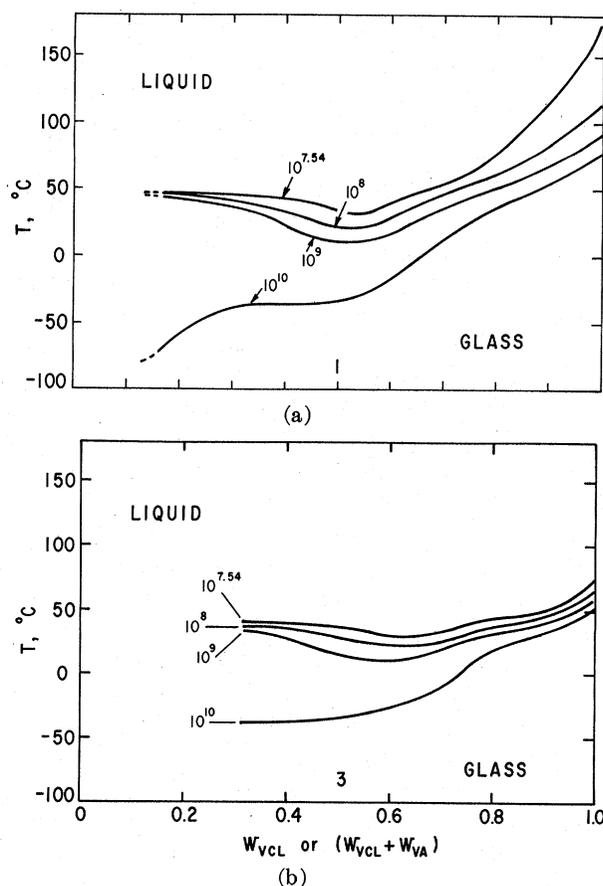


Fig. 6 (continued)

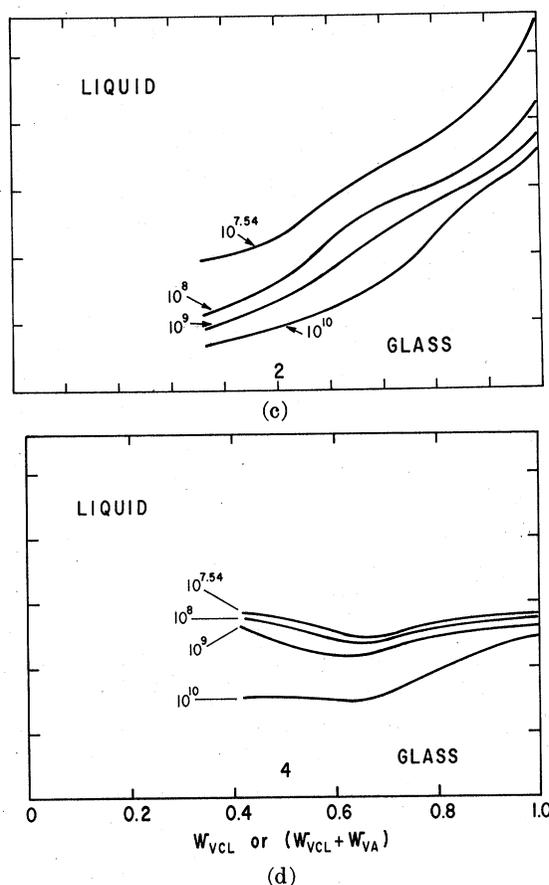


Fig. 6. Isochronal temperature-composition diagrams for mixtures and for selected copolymers and terpolymers: (a) copolymers of vinyl stearate and vinyl chloride; (b) mixtures of poly(vinyl chloride) and di-2-ethylhexyl phthalate (DOP); (c) terpolymers containing 0.60 mole fraction of vinyl chloride (d) terpolymers containing 0.20 mole fraction of vinyl chloride.

These values lie between temperature differences found by Yannas³² for gelatin-glycerol mixtures and by Tobolsky³ for poly(vinyl chloride) and several external plasticizers. This correlation is similar to that found for copolymers of the *n*-alkyl acrylates and methyl methacrylate.¹⁷ Consequently, rough estimates of T_g may be obtained from mechanical data using eq. (8).

It might be worthwhile here to mention the generally poor correlation found between the flex temperature T_f of the Clash-Berg measurement¹⁹ and T_g in recent studies.^{1,17} T_f values are taken at a constant modulus of 0.931×10^{10} dynes/cm². In line with the vertical downward displacement of glassy modulus at high vinyl stearate content, as expressed by the magnitude of the parameters of eq. (1), T_f was found to occur at temperatures progressively further below T_g at higher weight fractions of fatty comonomers.

The difference in the two temperatures became extreme as side-chain crystallinity acted to raise the apparent T_g . Similar behavior was reported recently.^{1,17} It may be responsible for the seeming anomalous¹⁶ relation found between $1/T_f$ and the mole fraction of the N-*n*-alkylacrylamides in copolymers with acrylonitrile³³ and for the unexpectedly low T_f values of the analogous copolymers with vinylidene chloride.³⁴ As this paper and another¹⁷ demonstrate, correlations with T_i are generally, though not always,¹⁸ more dependable than those with T_f .

CONCLUSIONS

Isochronal modulus-temperature curves for the internally plasticized systems of this paper were presented in a form permitting direct comparison with similar quantities in the literature for poly(vinyl chloride) plasticized by a variety of external plasticizers. Comparison was made in this paper with data for poly(vinyl chloride) plasticized by DOP. The data revealed that moduli of the copolymers and terpolymers reached the low values of soft polymers at room temperature, only through a short range of composition, before being raised by side-chain crystallinity. This crystallinity produced undesirably brittle compositions. In contrast, main-chain crystallinity, present in the externally plasticized poly(vinyl chloride) compositions, raised moduli and produced a desirably broad use temperature range and superior ultimate properties. It is apparent from the overall results that further modification of these internally plasticized systems will be required to develop a completely nonvolatile plasticized system of practical utility.

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References

1. E. F. Jordan, Jr., B. Artymyshyn, G. R. Riser, J. Nidock, and A. N. Wrigley, *J. Appl. Polym. Sci.*, **17**, 1541 (1973).
2. A. T. Walter, *J. Polym. Sci.*, **12**, 207 (1954).
3. R. B. Taylor and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **8**, 1563 (1964).
4. M. C. Shen and A. V. Tobolsky, *Advan. Chem. Ser.*, **48**, 118 (1965).
5. N. Hata and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **12**, 2597 (1968).
6. A. V. Tobolsky, D. Carlson, and N. Indictor, *J. Appl. Polym. Sci.*, **7**, 393 (1963).
7. R. Sabia and F. R. Eirich, *J. Polym. Sci. A*, **1**, 2497 (1963).
8. R. Sabia and F. R. Eirich, *J. Polym. Sci. A*, **1**, 2511 (1963).
9. T. Alfrey, Jr., M. Wiederhorn, R. Stein, and A. V. Tobolsky, *J. Colloid Sci.*, **4**, 211 (1949).
10. S. A. Iobst and J. A. Manson, *Polym. Prepr.*, **11**(2), 765 (1970).
11. R. A. Acosta, J. A. Manson, S. A. Iobst, *Polym. Prepr.*, **12**(2), 745 (1971).
12. L. Mandelkern, *Crystallization in Polymers*, McGraw-Hill, New York, 1964, pp. 74-116.
13. G. Kraus, K. W. Rollmann, and J. T. Gruver, *Rubber Chem. Technol.*, **44**, 598 (1971).
14. E. F. Jordan, Jr., D. W. Feldeisen, and A. N. Wrigley, *J. Polym. Sci. A-1*, **9**, 1835 (1971).

15. E. F. Jordan Jr., B. Artymyshyn, A. Specca, and A. N. Wrigley, *J. Polym. Sci. A-1*, **9**, 3349 (1971).
16. E. F. Jordan, Jr., *J. Polym. Sci. A-1*, **9**, 3367 (1971).
17. E. F. Jordan, Jr., G. R. Riser, B. Artymyshyn, J. Pensabene, and A. N. Wrigley, *J. Polym. Sci., A-2*, **10**, 1657 (1972).
18. E. F. Jordan, Jr., G. R. Riser, C. Salber, and A. N. Wrigley, *J. Appl. Polym. Sci.*, **16**, 3017 (1972).
19. R. F. Clash, Jr., and R. M. Berg, *Ind. Eng. Chem.*, **34**, 1218 (1942).
20. S. D. Gehman, D. E. Woodford, C. S. Wilkinson, Jr., *Ind. Eng. Chem.*, **39**, 1108 (1947).
21. J. B. Yannas and A. V. Tobolsky, *J. Macromol. Chem.*, **1**, 399 (1966).
22. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, pp. 356-407.
23. R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).
24. M. C. Shen and A. Eisenberg, *Rubber Chem. Technol.*, **43**, 146-148 (1970).
25. E. Butta and P. L. Magagnini, *Ann. Chim. (Rome)*, **53**, 1034 (1963).
26. P. I. Vincent, in *Encyclopedia of Polymer Science and Technology*, Vol. 7, M. F. Mark, N. G. Gaylord, and N. Bikales, Eds., Interscience, New York, 1967, p. 292.
27. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, (a) pp. 172-177; (b) pp. 189-191; (c) pp. 183-184.
28. P. R. Saunders and J. D. Ferry, *J. Colloid Sci.*, **14**, 239 (1959).
29. I. Sakurada, T. Ito and K. Nakamae, *J. Polym. Sci. C*, **15**, 75 (1966).
30. J. R. Joseph, J. L. Kardos, and L. E. Nielsen, *J. Appl. Polym. Sci.*, **12**, 1151 (1968).
31. I. Yannas, *J. Polym. Sci. A-2*, **6**, 687 (1968).
32. J. B. Yannas and A. V. Tobolsky, *J. Macromol. Chem.*, **1**, 723 (1966).
33. E. F. Jordan, Jr., G. R. Riser, W. E. Parker and A. N. Wrigley, *J. Polym. Sci., A-2*, **4**, 975 (1966).
34. E. F. Jordan, Jr., G. R. Riser, B. Artymyshyn, W. E. Parker, J. W. Pensabene, and A. N. Wrigley, *J. Appl. Polym. Sci.*, **13**, 1777 (1969).