High-Temperature Mechanical Behavior of PVC: A Comparison of Suspension- and Emulsion-Prepared Polymers

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Synopsis

We have investigated the high temperature mechanical behavior of several unplasticized emulsion- and suspension-prepared whole polymers, and carried out molecular weight, molecular weight distribution, and branching characterization studies on these same materials. It is concluded that the easier workability of the emulsion product is probably due to the absence of a considerable amount of high molecular weight polymer in these as compared to suspension-prepared polymers of equal average molecular weight as reflected by intrinsic viscosity determinations of Fikentscher K values.

Introduction

The two industrially important processes for the polymerization of vinyl chloride are those carried out in suspension and in emulsion. As is well known, these two processes yield polymers that differ markedly in their workability; in particular, the unplasticized material prepared in emulsion lends itself to molding and extrusion more readily than does the corresponding polymer (of equal molecular weight) prepared in suspension. This difference, as well as other physical dissimilarities such as absorption and diffusion rates, are generally attributed to residual quantities of emulsifying agents. More recently, however, these latter differences at least have been shown to persist even after appropriate extraction.[1]

It is reasonable to assume that the quality of workability should be reflected in a polymer's bulk viscoelastic properties. We investigated three vinyl chloride whole polymers: two suspensions-prepared products and an emulsion-prepared product having a Fikentscher K value[2] equal to that of one of the suspension polymers. Their high-temperature stress relaxation behavior was examined and correlated with results of determinations of molecular weight distribution, higher order average molecular weight, and certain chemical and physical tests designed to reveal differences in branching.

Experimental

The three polymers studied were as follows. Suspension A (S-A) was a suspension-prepared, unplasticized whole polymer having $K = 66$ (suspending agent, methyl cellulose; dispersing liquid, water; 50°C; lauroyl peroxide as initiator).

Suspension B (S-B) was a suspension-prepared unplasticized whole polymer having $K = 52$ [suspending agent, methyl cellulose or poly(vinyl alcohol); dispersing liquid, water; 65°C; lauroyl peroxide as initiator].

Emulsion A (E-A) was an emulsion-prepared, unplasticized whole polymer having $K = 66$ (typical emulsifying agent; dispersing liquid, water; 50°C; persulfate redox system as initiator) containing less than 0.2% water-extractable material.

Otherwise the three polymers appeared to be free of impurities, at least within the analytical limits of infrared examination.

To the polymers, which were about three years old, was added 3% by weight of stabilizers (two parts dibasic lead stearate to one part dibutyltin ethylhexoate) by calendaring the mixture for 5 minutes at 190°C. The compositions were then molded into thin 0.5 mm sheets by heating at a temperature of 200°C for 5 min, then applying a pressure of 40 kg/cm², and letting them cool under pressure for 15–20 min. The sheets were subsequently die cut into dog-bone samples, 2.55 mm in width and 50 mm in gage length. The samples were conditioned for a period of 15 min at the particular test temperature prior to each experiment.

The average molecular weights of the samples used were checked before and after the higher-temperature measurements to ascertain the efficiency of the stabilizer system and the results observed, (a slight increase in molecular weight assured us that the polymers were not appreciably altered by the tests themselves).

The polymers were investigated through: (1) a series of standard materials properties test in their glassy condition at 23°C and 50% R H; (2) uniaxial stress relaxation measurements at temperatures between 100°C and 175°C for a time span of 0.01–3600 sec carried out on a device previously reported by us;[3] (3) a determination of their molecular weight distribution curves by the analysis of sedimentation boundary spreading on ultracentrifugation, recently applied to poly(vinyl chloride) in this Institute;[4] (4) ultracentrifugation of mixtures of the emulsion and suspension products of equal average molecular weight; (5) dehydrochlorination experiments in atmospheres of nitrogen and of oxygen. In these last studies, a stream of preheated gas is passed over the degrading polymer and the vapors liberated are thus transported to and absorbed by a 1% aqueous solution of KCl. The amount of HCl developed from the polymer is determined by the variation in the pH of this solution.

Results

A comparison of the glasslike properties of the three polymers studied is given in Table I, while Figure 1 presents representative views (electron

Suspension A
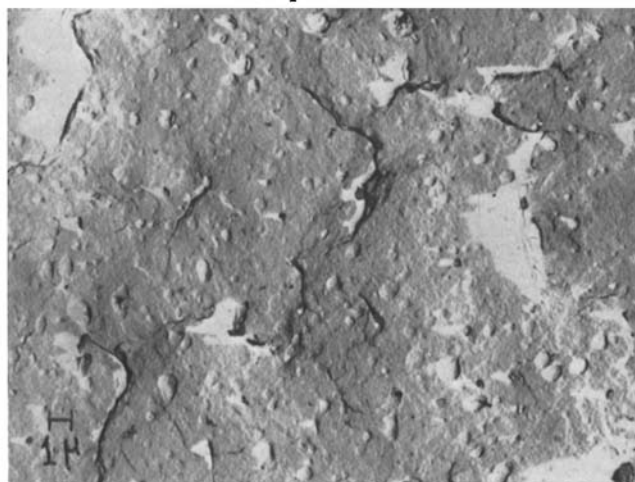
Emulsion A

Fig. 1. Electron micrographs of fracture surface replicas: (*a*) suspension A (S–A); (*b*) emulsion A (E–A).

micrograph replicas) of the fracture surfaces formed in S-A and E-A by the Izod impact test. The only observations apparent from the photographs are that the emulsion polymer shows a more irregular fracture path and the presence of a somewhat greater number and size of what appear to be voids.

Figures 2, 3, and 4 show the relaxation data and indicate that they are all fairly well represented by functions of the type $E_r(t) = At^\alpha$. For a more complete comparison the suspension A and emulsion A relaxation experiments were carried out at the same strain $\epsilon = (l - l_0)/l_0 = 0.4$ with the exception of the 160 and 170°C tests on emulsion A, which instead were performed at $\epsilon = 0.1$ because at these higher temperatures the sample E-A broke at a higher strain in times of the order of 1 sec following the

TABLE I
Glassy State Properties Determined at 23°C, 50% RH

Property	Suspension A	Suspension B	Emulsion A
Elastic modulus (flexure), kg/cm²	31500	30000	31000
Breaking stress (final area), kg/cm²	1400	1400	1550
Yield stress, kg/cm²	565	575	580
Elongation to break, %	170	140	170
Impact (Izod notch), kg-cm/cm	4.0	3.5	5.1
Hardness (Rockwell)	L97	L98	L95
Softening (Vicat, 5 kg), °C	82.7	80.5	84.1
Elastic modulus (flexure 800 cps), kg/cm²	31762	31561	34250
Loss tangent (Q^{-1})	4.76×10^{-2}	4.30×10^{-2}	4.75×10^{-2}
Density (column at $T = 20°C$), g/cm³	1.40_5	1.40_0	1.40_0

elongation. Therefore another observation is that the emulsion polymer ruptures at lower strains at high temperatures than does the suspension product of equal average molecular weight. The S-B experiments were performed at $\epsilon = 0.2$ for the same reason. We tried to investigate the anomaly noted in the stress relaxation of S-B at 160°C, i.e., the upswing at longer times. Measurement of the molecular weight of the sample showed that this quantity was not altered. A possible explanation might be the onset of recrystallization under the combined effects of temperature and elongation, once stress equilibrium is achieved in the structure. No such variations in crystallinity were observable under x-ray examination, but this might be due to the low order of crystallinity.

Figure 5 presents the apparent master curves of the three polymers referred to a temperature of 130°C. Table II catalogs the various stress relaxation functions, distributions of relaxation times, cumulative viscosi-
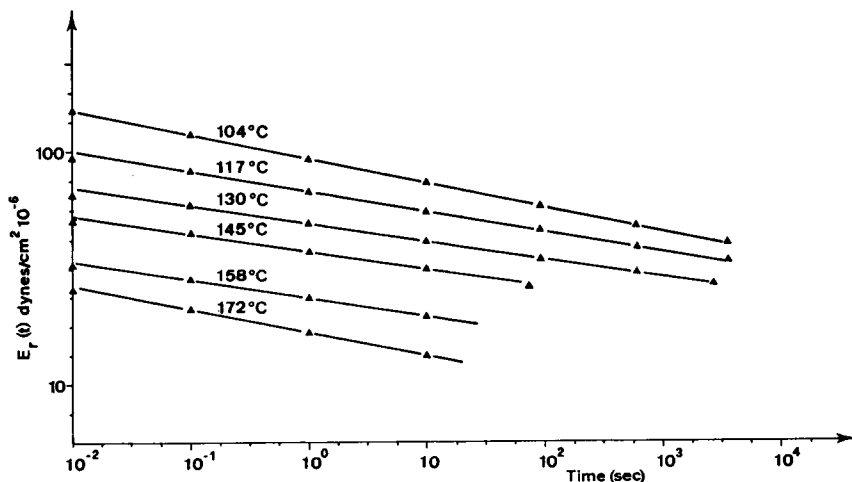

Fig. 2. Stress relaxation data $E_r(t)$ of sample S-A.

ties,[3] and shift factors found for the different temperatures. The distribution of relaxation times and cumulative viscosities were obtained by application of the eq. (1) and (2), respectively:

$$E_r(t) = \int_0^\infty E(\tau)e^{-t/\tau}\, d\tau \tag{1}$$

$$\eta_T(t') = \int_t^{t'} E_r(t)dt \tag{2}$$

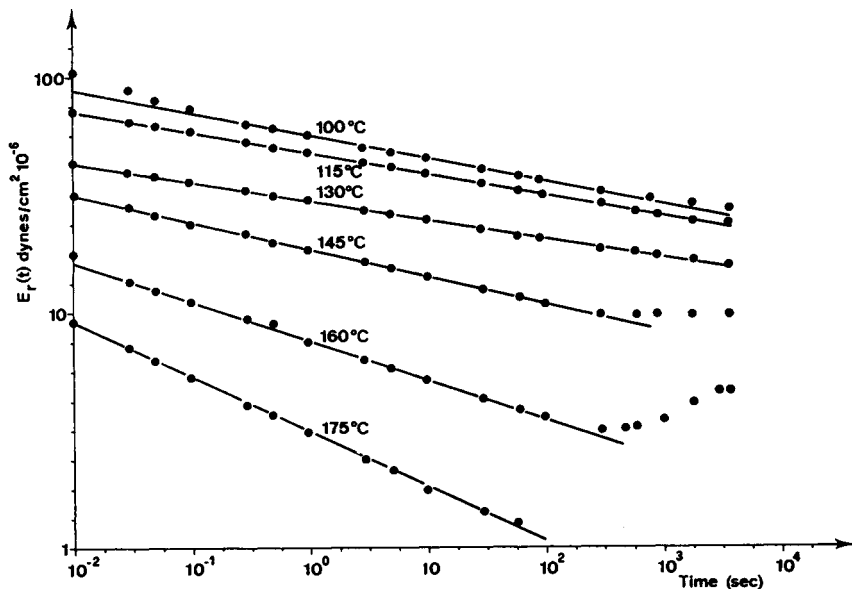where η_T (tensile viscosity) $= \eta$ (shear) $2(1 + \mu)$.

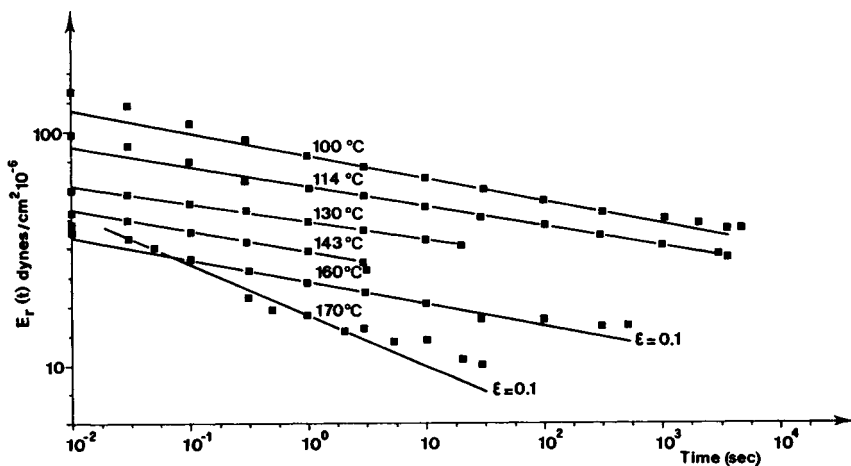Fig. 3. Stress relaxation data $E_r(t)$ of sample S-B.

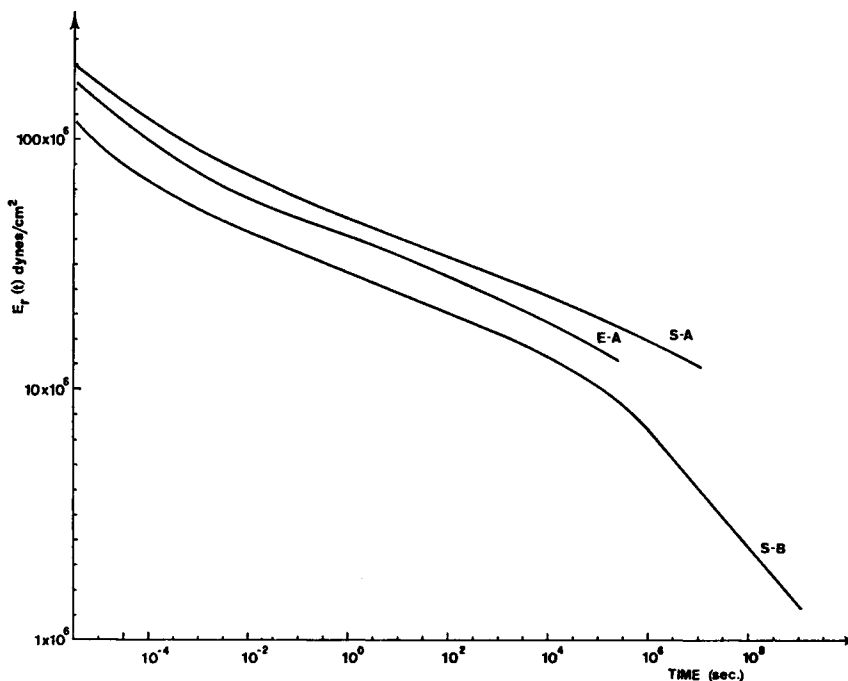Fig. 4. Stress relaxation data $E_r(t)$ of sample E-A.

Fig. 5. Apparent master curves at 130°C.

Employing the a_T's listed, we estimated the activation energy of the molecular phenomena governing this shift factor as 80 kcal/mole for S-A, 100 kcal/mole for S-B, and 102 kcal/mole for E-A (145°C and lower).

These commercial-type polymers of vinyl chloride are believed to be about 5–10% crystalline.[5,6] It has also been suggested that this phase or these regions of relatively high molecular order effectively crosslink the polymer above its glass temperature, preventing any truly viscous flow and giving rise instead to a broad rubbery temperature region.

This was in fact seen to be the case in an earlier study.[3] Further, the change in crystallinity can be detected by the polymers' infrared spectrum, specifically from the ratio of absorbances at 635 and 693 cm^{-1}.[7,8] This ratio is plotted as a function of temperature in Figure 6 and indicates that the two polymers of higher molecular weight, S-A and E-A, are of about the same crystallinity and also that its change with temperature is the same. Figure 7 plots the different shift factors and also the corresponding WLF equation. The ever increasing deviations with increasing temperature again testify to a changing polymer structure.

Figure 8 shows the molecular weight distribution of the three polymers studied and reveals that the make-up of the two polymers of higher molecular weight is quite different, e.g., S-A has 10% of material having a molecular weight equal to or greater than 200000, while E-A has only about 1%. Table III catalogs the various higher order average molecular weight

TABLE II
Viscoelastic Functions

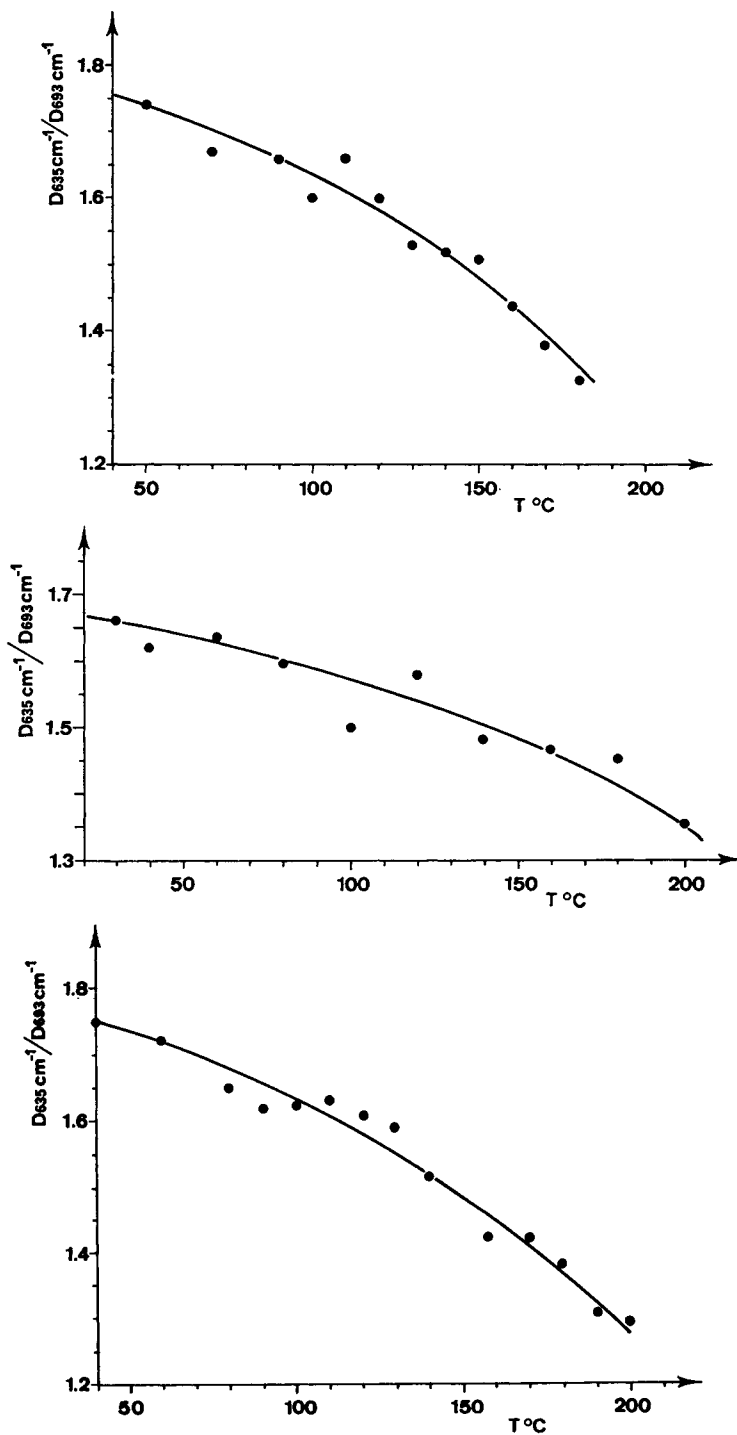| T, °C	$E_r(t)$, dyne/cm²	$\eta(t)$, poise	$H(\tau) \equiv \tau E(\tau)$	a_T (apparent)
Suspension				
A				
104	$85.0 \times 10^4 t^{-0.117}$	$96.3 \times 10^4 t^{0.883}$	$10.52 \times 10^5 \tau^{-0.117}$	806
117	$66.7 \times 10^4 t^{-0.088}$	$73.1 \times 10^4 t^{0.912}$	$6.14 \times 10^5 \tau^{-0.088}$	47.6
130	$49.0 \times 10^4 t^{-0.084}$	$53.5 \times 10^4 t^{0.916}$	$4.35 \times 10^5 \tau^{-0.084}$	1.0
145	$37.4 \times 10^4 t^{-0.076}$	$40.5 \times 10^4 t^{0.924}$	$2.96 \times 10^5 \tau^{-0.076}$	1.96×10^{-2}
158	$23.5 \times 10^4 t^{-0.084}$	$25.6 \times 10^4 t^{0.916}$	$2.08 \times 10^5 \tau^{-0.084}$	4.35×10^{-6}
172	$16.8 \times 10^4 t^{-0.102}$	$18.7 \times 10^4 t^{0.898}$	$1.803 \times 10^5 \tau^{-0.102}$	7.35×10^{-7}
Suspension				
B				
100	$55.3 \times 10^4 t^{-0.0994}$	$61.4 \times 10^4 t^{0.901}$	$5.82 \times 10^5 \tau^{-0.0994}$	2626
115	$46.6 \times 10^4 t^{-0.090}$	$51.2 \times 10^4 t^{0.910}$	$4.39 \times 10^5 \tau^{-0.090}$	264.6
130	$29.8 \times 10^4 t^{-0.0799}$	$32.4 \times 10^4 t^{0.920}$	$2.48 \times 10^5 \tau^{-0.0799}$	1.0
145	$18.4 \times 10^4 t^{-0.116}$	$20.8 \times 10^4 t^{0.884}$	$2.26 \times 10^5 \tau^{-0.116}$	1.223×10^{-3}
160	$7.67 \times 10^4 t^{-0.166}$	$9.20 \times 10^4 t^{0.834}$	$1.37 \times 10^5 \tau^{-0.166}$	1.167×10^{-6}
175	$3.06 \times 10^4 t^{-0.234}$	$3.99 \times 10^4 t^{0.766}$	$0.786 \times 10^5 \tau^{-0.234}$	2.269×10^{-8}
Emulsion				
A				
100	$79.5 \times 10^4 t^{-0.0941}$	$87.7 \times 10^4 t^{0.9059}$	$7.86 \times 10^5 \tau^{-0.0941}$	2500
114	$58.0 \times 10^4 t^{-0.0854}$	$63.5 \times 10^4 t^{0.9146}$	$5.16 \times 10^5 \tau^{-0.0854}$	129.8
130	$41.4 \times 10^4 t^{-0.0774}$	$44.9 \times 10^4 t^{0.9226}$	$3.32 \times 10^5 \tau^{-0.0774}$	1.0
143	$30.4 \times 10^4 t^{-0.0908}$	$33.4 \times 10^4 t^{0.9092}$	$2.91 \times 10^5 \tau^{-0.0908}$	1.362×10^{-2}
160	$22.8 \times 10^4 t^{-0.095}$	$25.2 \times 10^4 t^{0.905}$	$2.28 \times 10^5 \tau^{-0.095}$	4.16×10^{-4}
170	$16.4 \times 10^4 t^{-0.223}$	$21.1 \times 10^4 t^{0.777}$	$4.01 \times 10^5 \tau^{-0.223}$	8.14×10^{-4}

Fig. 6. Crystallinity index as a function of temperature: (a) S-A; (b) S-B; (c) E-A.
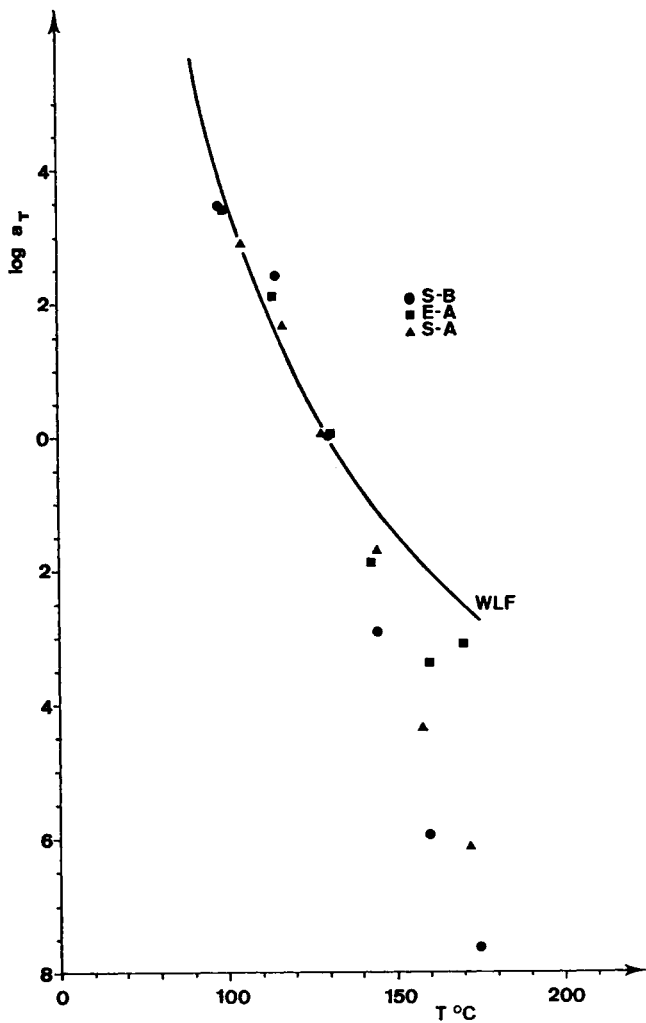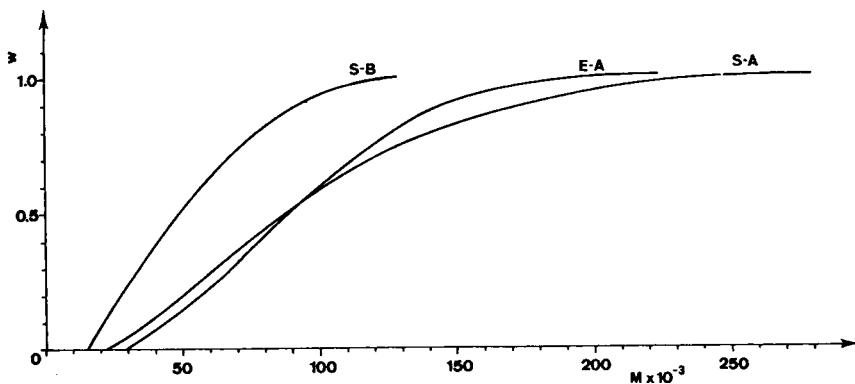
Fig. 7. Shift factors observed vs. WLF equation.

Fig. 8. Molecular weight distributions.

TABLE III
Various Average Molecular Weights

	Suspension A	Suspension B	Emulsion A
Calculated from MWD curves (polymer before molding)			
$\bar{M}_n$	69,600	40,300	76,000
$\bar{M}_v$	95,200	53,000	93,000
$\bar{M}_w$	98,600	55,000	95,000
$\bar{M}_z$	129,600	72,500	113,000
$\bar{M}_{z+1}$	156,000	87,200	130,000
$\bar{M}_w/\bar{M}_n$	1.4	1.4	1.3
Determined by viscometry (molded samples)			
$[\eta]$ at 25°C, ml/g			
$[\eta]_{cyclohex}$	102	69	102
$[\eta]_{THF}$	120	68	108
$\bar{M}_v{}^a$	113,000	53,500	98,000

a Data of Freeman and Manning (9).

calculated from the distribution curves, the intrinsic viscosity in cyclo-hexanone and $\bar{M}_v$ determined viscometrically from a published $[\eta]$–M equation in tetrahydrofuran.

On the basis of Kharasch's work,[10] Parker[11] is of the opinion that branches in PVC can occur only on carbon atoms carrying chlorine. The presence of the resulting tertiary chlorine has been postulated in a number of publications.[11-14] It would follow that the dehydrochlorination rate of a branched polymer in an inert atmosphere should depend on the number of tertiary chlorines present. Such experiments were recently carried out in this Institute;[15] the results are reported in Table IV, where we also list results of infrared determinations of the 540 cm^{-1} absorption band. These latter would indicate a higher concentration of tertiary chlorines in the emulsion polymer; however, as pointed out by Shipman et al.,[16] the 540 cm^{-1} absorption can not unequivocably be assigned to the tertiary Cl.

Finally we looked for differences in chain branching following a suggestion of Moore and Adcock,[17] who affirm that linear and branched species of polymers may be separated on the basis of differences in sedimentation rates

TABLE IV
Dehydrochlorination Studies[a]

Polymer	Degradation velocity, (mole HCl/g polymer/min)		Infrared absorbance (540 cm^{-1}), mm^{-1}
	Under N$_2$ (99.999% pure)	Under O$_2$	
Suspension A	0.163	0.697	0.82
Suspension B	0.214	0.651	0.95
Emulsion A	0.257	0.587	1.42

a T = 71°C; gas flow 112 cm^3/min.

in the ultracentrifuge: the sedimentation rate of the branched species should be accentuated by a reduction in its volume in solution. Such experiments on mixtures of S-A and E-A, however, failed to reveal any such differences.

Discussion and Conclusion

We see from the relaxation data as summarized in Table II that the suspension polymer S-A exhibits moduli, relaxation times, and bulk viscosities significantly higher than those of an emulsion product E-A having identical intrinsic viscosity (Table III). If we do not consider the possible role of the voids evident in the electron micrographs (which we hope to look into more completely in a future paper), we are left with two possible explanations for these differences.

We have already shown that the partial crystalline nature of PVC physically crosslinks this polymer when in its rubbery state.[3] This material could therefore be expected to follow the equation of rubber elasticity:

$$\sigma = \nu_e kT(\alpha - \alpha^{-2})$$

where σ is the stress based on the original cross section and ν_e is the density of load-bearing chains. Figure 9 plots the apparent ν_e at 1 sec as a function of test temperature for each of the polymer studied. If the primary network is attributed to uniformly dispersed crystallites, ν_e must be equal to ν (the number of segments introduced by these crystallites which for the more usual network structure has been shown experimentally by Flory[18] and more recently analytically by Scalon[19] to be essentially independent of the
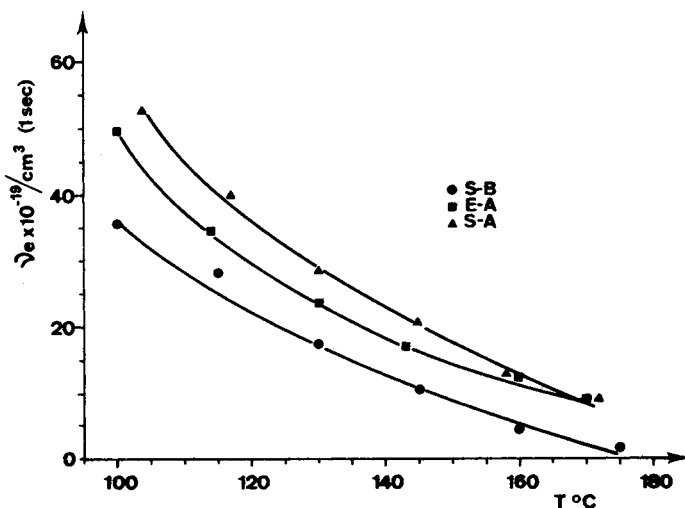

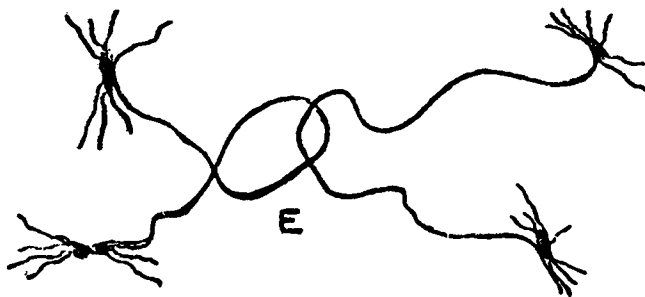Fig. 9. Apparent ν_e at 1 sec as a function of temperature.

Figure 10.

molecular weight distribution) plus ν_T (additional segments resulting from entanglement points) less ν_c (density of chain ends, i.e., nonload-bearing segments). If, as the crystallinity data of Figure 6 seem to indicate, the two polymers S-A and E-A are the same in ν, then the differences observed in ν_e can only be due to (1) a greater number of nonload-bearing chains in E-A, e.g., from branching; (2) a greater number of entanglements points in S-A, or a combination of these effects.

Since we do not have any direct, uncontestable evidence of differences in chain branching and instead have observed a significant difference in the amount of high weight material present in the two polymers, let us proceed with a more detailed consideration of entanglement effects. These contribute to the network only if they are in segments bounded by more permanent type links on both ends, as pictured in Figure 10.[20]

As a consequence, their contribution in general should be greater, the greater the number of primary links.[20] In our present picture the primary links are the postulated crystallites. This interpretation or explanation of the differences observed in the high-temperature mechanical behavior of the suspension and emulsion prepared polymers could also account for the lessening of these differences at the higher temperatures (see Fig. 9) by the elimination of entanglement contributions to the supporting network structure by the gradual break-up of the surrounding crystallites.

The practical conclusion is that the better workability of the polymer prepared in emulsion compared to that of a polymer of equal Fikentscher K prepared in suspension is probably due to the smaller quantity of high molecular weight species in the former.

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