Viscoelastic Properties of Plasticized Poly(vinyl Chloride)

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Synopsis

Master curves in stress relaxation for several samples of poly(vinyl chloride) plasticized by varying proportions of dioctyl phthalate [di(2-ethylhexyl phthalate)] are reported and discussed in terms of plasticizer concentration and polymer structure.   Modulus–temperature curves derived from the data are also shown.   Comparisons are given of plasticized compositions of poly(vinyl chloride) and polystyrene.   The useful commercial properties of poly(vinyl chloride) are discussed in the light of data on the polymer structure and plasticizer action.

INTRODUCTION

Because of its widespread use as a fabricating material, considerable work has been done on several aspects of the mechanical properties of both plasticized and unplasticized poly(vinyl chloride).   Studies of the creep behavior have been made by several workers.[1–5]   The general information gained from these indicates that poly(vinyl chloride) cannot be regarded as a typical amorphous polymer such as polystyrene or poly(methyl methacrylate).   Early suggestions that this polymer is crosslinked chemically have been discarded in favor of a semicrystalline structure, the degree of crystallinity being sufficiently small for the individual crystallites to act as more or less rigid crosslinks.

Many investigations of the mechanical properties of poly(vinyl chloride) compositions have been designed in order to study the mechanism of plasticizer action both from the point of view of plasticizer concentration and chemical nature of the plasticizer.[6]   In the present work it was decided to investigate the time-dependent relaxation modulus of poly(vinyl chloride), both unplasticized and plasticized, and to compare this with similar data for other polymers, the structures of which are more fully understood. Such a study should provide information on the viscoelastic behavior of poly(vinyl chloride) itself as well as on the effects produced in this polymer by various proportions of low molecular weight plasticizer.

EXPERIMENTAL

The samples of poly(vinyl chloride) used in this work were supplied by Monsanto Chemical Co. and Allied Chemical Co.   The polystyrene sam-

ples were furnished by Kopper's Co. Inc. Two series of compositions were employed. Poly(vinyl chloride) samples plasticized with di(2-ethylhexyl phthalate), referred to below as dioctyl phthalate (DOP), over a weight percentage range of 0 to 44 were used to study the effect of plasticizer concentration on the mechanical properties. In addition, poly(vinyl chloride) plasticized with 16% of ethyl hexyl phosphate was examined in order to compare the behavior with that of a sample of similarly plasticized polystyrene, this being a typical example of a completely amorphous polymer. The molecular weights of the polymers were 3×10^5 for the polystyrene and 5×10^4 for the poly(vinyl chloride), as determined by viscosity measurements in dilute solution.

Two types of measurements were made on these samples in order to determine the variation of modulus with time. For the region of modulus below 10^4 dynes/cm.^{2}, a stress relaxation balance was employed in which a constant small strain was applied at zero time and the variation of stress was followed as a function of time at constant temperature. For moduli above 10^9 dynes/cm.^{2} a Clash-Berg[10] torsional creep apparatus was used. This consists of applying a known torque to a sample and measuring the angle of twist produced. The Clash-Berg apparatus yields the shear creep compliance $J_c(t)$. To convert this to shear relaxation modulus the expression

$$G_r(t) = \sin m\pi/m\pi \, J_c(t) \tag{1}$$

was used, where m is the slope of the double logarithmic plot of $J_c(t)$ versus time. Stress relaxation measurements yield the tensile relaxation modulus $E_r(t)$. At low moduli, i.e., below 10^9 dynes/cm.^{2}, where the Poisson ratio for most materials is 0.5

$$E_r(t) = 3G_r(t) \tag{2}$$

In order, therefore, to combine the two types of measurements to cover the whole range in modulus the results are expressed as $3G_r(t)$.

The samples measured were in the form of rectangular strips, and sufficient numbers of samples were prepared and annealed above the glass transition temperature to make measurements at a series of temperatures for the particular composition.

RESULTS

Modulus–time curves at various temperatures were obtained for poly(vinyl chloride) compositions having six different concentrations of dioctyl phthalate. Usually measurements were made at sufficiently high and low temperatures so that the highest modulus approached the glassy plateau and the lower values approached the rubbery plateau region. In this way the transition region could be covered in some detail. For the unplasticized poly(vinyl chloride) a sufficient range in temperature was covered so that both the glassy modulus and the rubbery plateau could be clearly
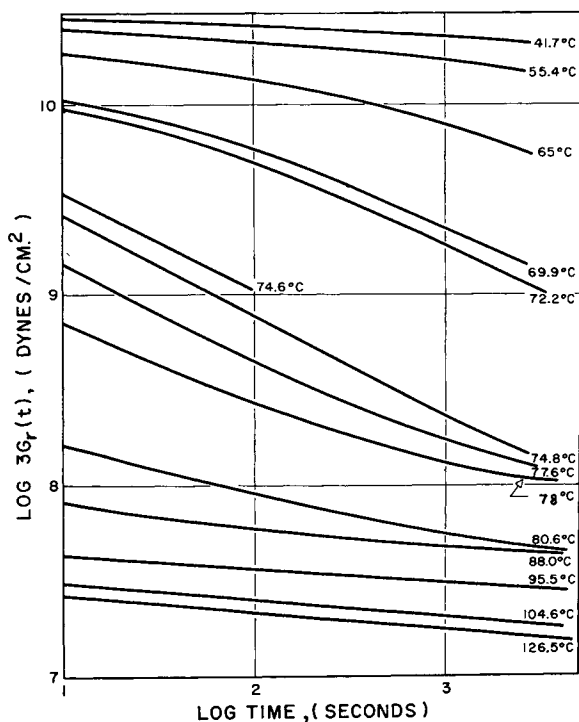
Fig. 1. Modulus–time curves for unplasticized poly(vinyl chloride) at various temperatures.

observed. These curves are shown in Figure 1 and may be taken as representative of the results obtained for all the other systems.

In order to obtain the master curves for these compositions, the time–temperature superposition principle was utilized in which the curves of Figure 1 may be shifted horizontally along the log time axis with respect to one fixed curve, the temperature corresponding to this curve being taken as the reference temperature. The use of this method has been largely accepted for linear amorphous polymers, the morphology of which does not change over the temperature range studied, but has been found inapplicable to crystalline polymers such as polyethylene.[7] This presumably is due to the effect of the degree of crystallinity changing with temperature. In the present study of what has been classed as a semicrystalline polymer, the curves obtained seemed to be adequately superimposable, so that the use of the time–temperature superposition principle was felt to be justified.

The method used to describe the temperature dependence of the viscoelastic process was as follows. The characteristic relaxation time $K(T)$, arbitrarily defined as the time required for the stress in the material to relax to a modulus value of $3G_r(t) = 10^9$ dynes/cm.[2], was determined. This was obtained either directly from plots such as Figure 1 or by moving the
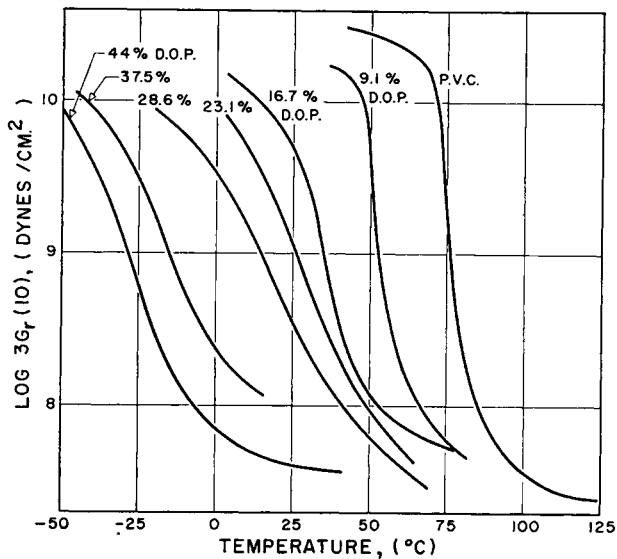
Fig. 2. Modulus–temperature curves for poly(vinyl chloride) and samples plasticized with dioctyl phthalate.

curves horizontally to obtain superposition and measuring the displacement required on the time scale. An arbitrary temperature was selected as the temperature at which the characteristic relaxation time was 10 sec. This temperature has been defined in previous studies[8] as T_i and usually lies within a few degrees of the glass transition temperature.[9] The effect of temperature on the characteristic relaxation time will be discussed in terms of the WLF equation below.

A useful source of information on the viscoelastic behavior of polymers is the variation of modulus, usually a 10-sec. modulus, with temperature. Such modulus temperature curves in many ways show the general type of master curve expected for a particular polymer. Such information is usually obtained by use of Clash-Berg[10] and Gehman[11] techniques which yield shear modulus. In the present work using the modulus time curves at various temperatures as typified by Figure 1 the 10-sec. modulus was obtained by various temperatures by extrapolating the data to log $t = 1$. The curves produced are shown in Figure 2 for various concentrations of dioctyl phthalate in poly(vinyl chloride). From these curves the value of T_i as defined above and s, the slope of the curve at T_i, may be obtained. These parameters are listed in Table I. The value of this type of measurement lies in the comparison of data obtained for different polymer systems since the choice of a 10-sec. modulus is completely arbitrary, though relationships have been proposed between s and the slope of the master curve n.

The master curves of $3G_r(t)$ as a function of time for the samples of poly(vinyl chloride) plasticized with dioctyl phthalate are shown in Figure 3.

TABLE I

Composition		E_1, dynes/ cm.^{2} $\times$ 10^{-10}	E_2, dynes/ cm.^{2} $\times$ 10^{-7}	n	s	T_i, °C.	T_g, °C.
Polymer	Plasticizer						
PVC	None	4	2	−0.59	−0.23	77.6	81
"	9.1% DOP	3	2.5	−0.55	−0.19	52	53
"	16.7%	3.5	3	−0.48	−0.11	35	37
"	23.1% DOP	4	2	−0.33	−0.050	26	25
"	28.6% DOP	2.5	4	−0.30	−0.044	15	15
"	37.5% DOP	2	2	−0.27	−0.054	−14.2	−10
"	44.4% DOP	3	2.5	−0.31	−0.059	−33	−30
Polystyrene	16% EHP	—	—	−0.54	−0.15	47.5	—
PVC	16% EHP	—	—	−0.25	−0.084	42.6	45

The method of representing the data is to plot the master curves which were originally reduced to widely varying temperatures at the same position on the time scale. This involves a displacement of the curves relative to one another along the log time scale until the modulus value of 10^9 dynes/cm.^{2} corresponds to a time of 10 sec. The purpose of this is to indicate changes in the slope of the transition region as a function of dioctyl phthalate concentration. From these master curves several parameters may be obtained. The moduli in the glassy and rubbery regions E_1 and E_2 could not be measured directly due to the very broad transition regions observed in some of the more highly plasticized samples, the high temperatures required producing degradation and the low temperatures being experimentally inaccessible. As a substitute for direct measurement,
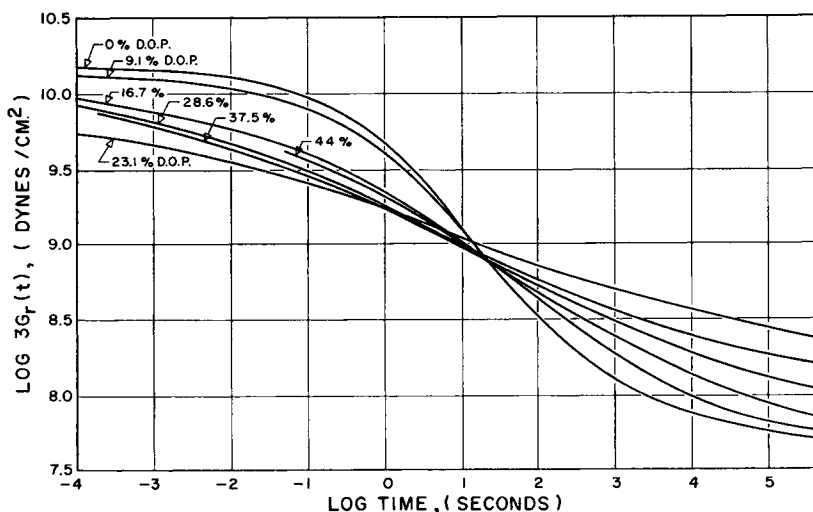

Fig. 3. Master curves of poly(vinyl chloride) samples plasticized by dioctyl phthalate.

the values of the slope of the master curves at a series of modulus values
were plotted as a function of modulus and the curves extrapolated to zero
slope. This it was felt would yield precise enough information to detect
any significant changes in these quantities. The slope of the master curve
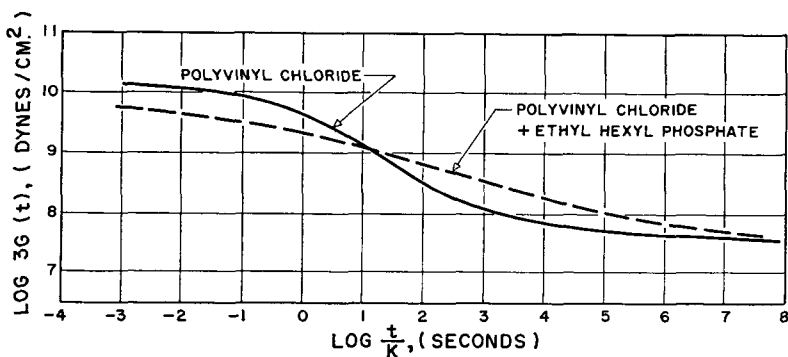n at the inflection point was obtained for all the compositions and was

Fig. 4. Master curves of poly(vinyl chloride) plasticized with ethyl hexyl phosphate and
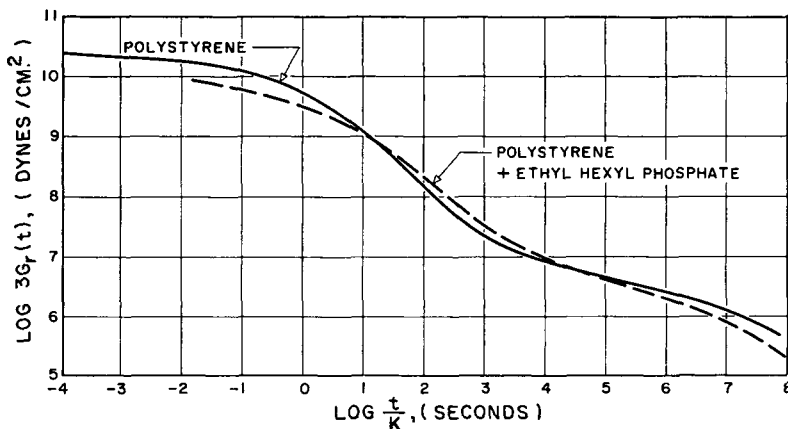of poly(vinyl chloride).

Fig. 5. Master curves of polystyrene plasticized with ethyl hexyl phosphate and of
polystyrene.

used as a measure of the breadth of the transition. The inflection tem-
perature is recorded together with the above parameters in Table I. Data
on poly(vinyl chloride) plasticized with 16% of ethyl hexyl phosphate are
shown in Figure 4; results on polystyrene plasticized with the same amount
of ethyl hexyl phosphate are given in Figure 5. The polystyrene master
curve[12] is included for comparison.

Values of T_g measured dilatometrically are also shown in Table I.

DISCUSSION

As indicated above, the structure of poly(vinyl chloride) is currently described as semicrystalline. The main evidence for this was obtained in an extensive experimental study of this polymer by birefringence, dilatometry, x-ray diffraction, and stress relaxation.[4,5] The degree of crystallinity, however, was apparently so slight that it could not be estimated quantitatively by any of the above techniques. At high temperatures (ca. 150°C.), the color of this polymer darkens, indicating decomposition. For this reason measurements were only made in the region where the polymer was known to undergo no rapid decomposition.

Master Curve of Unplasticized Poly(vinyl Chloride)

This master curve in Figure 4 is seen to show a glassy modulus of around 3×10^{10} dynes/cm.^{2}, followed by a transition region having a maximum slope of -0.59. This slope decreases gradually until the plot becomes almost linear with a very small negative slope. This slope is continued until decomposition occurs. This behavior is quite different from the behavior expected of a completely amorphous linear polymer where a further more rapid decrease in modulus to rubbery and liquid flow[3] regions is observed at long times. The general behavior shown in Figure 4 is very similar to that of a lightly crosslinked amorphous polymer[13] where chemical crosslinks prevent long-range rearrangements. That the material is crosslinked to a small extent, perhaps by the removal of hydrogen chloride during processing at high temperatures, is at first sight plausible if the hydrogen and chloride were abstracted from adjacent chains. The evidence from chemical decomposition, however, indicates that hydrogen chloride is re-
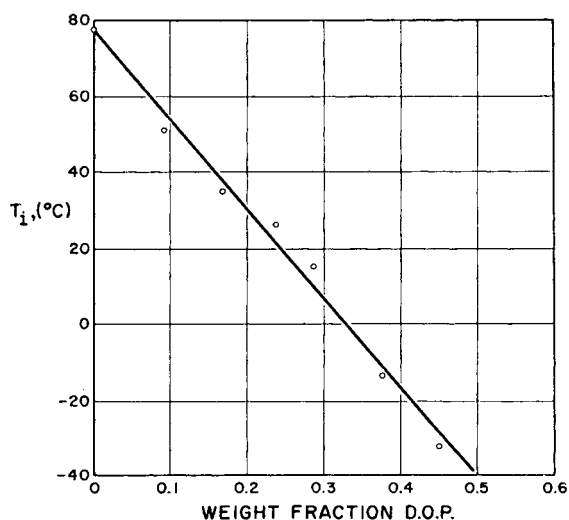

Fig. 6. Variation of inflection temperature with dioctyl phthalate concentration for poly(vinyl chloride).

moved from the same chain producing a polyene structure.[14] Some evidence for chemical crosslinking in presence of inorganic chlorides has been reported,[15] but such a mechanism would be unlikely in the present case. The samples used in this investigation were completely soluble in tetrahydrofuran at room temperature, indicating that the structure could not involve an appreciable degree of crosslinking. Also, attempts to increase the degree of crosslinking by heating as suggested by Doty and Zable[16] produced no resulting increase of modulus as would be expected if the crosslink density had been appreciably altered. From this evidence it should seem that the explanation of the long rubbery plateau must lie in the crystalline nature of the polymer. Definite proof of this could only be obtained by raising the temperature high enough for complete melting of the crystallites to occur. This temperature, estimated indirectly by Anagnostopoulos et al.[17] is 174°C. which is well above that at which the polymer begins to decompose.

Effect of Plasticizer

The effect of plasticizer on the master curves may be seen from figures 6 and 7 and from Table I.   The values of T_i are seen to decrease as plasticizer concentration increases.   The empirical equation[18]

$$T_i = T_i^0 - k\omega_1 \tag{3}$$

where T_i is taken close to T_g and ω_1 is the weight fraction of plasticizer has been found applicable at low values of ω_1.   This plot is shown in Figure 6 with $k = 230°$.

From Table I the limiting moduli E_1 and E_2 obtained as described above must be considered essentially constant.
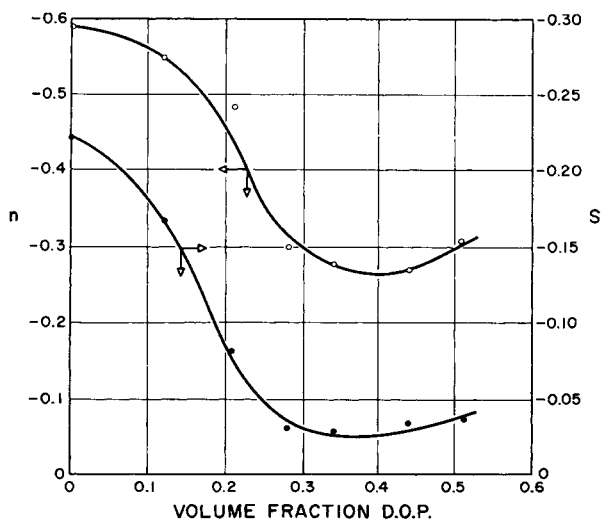

Fig. 7. Variation of slopes of master curves and modulus–temperature curves with dioctyl phthalate concentration for poly(vinyl chloride).

The most marked change observed in the master curve is the decrease in the slope of the transition region as plasticizer is added. The values of n are small compared to those for other polymers. For the plasticized samples n is much smaller than the theoretical slope of $-1/2$ in the lower transition region obtained from the Rouse[23] Bueche[24] theory. The slope n decreases until a value fraction of plasticizer of around 0.4 is reached, above which a small increase is observed. Similar changes are also observed in the slope s of the modulus–temperature curve in Figure 7. Nielsen et al.[1] found similar results when measuring the half width of the electrical damping peak as a function of plasticizer concentration. The maximum half width was also found to occur in the region of 0.4 volume fraction of plasticizer. This result would indicate that when this fraction of plasticizer is exceeded there may be some aggregation of plasticizer, reducing the efficiency. It would be expected from this idea, therefore, that some deviation from linearity would be observed for the variation of T_i with plasticizer concentration. As seen from Figure 6, within the limits of error no significant change is evident.

Discussion of the mechanism by which plasticizer alters the properties of poly(vinyl chloride) has been given by Alfrey et al.,[5] the effects being interpreted in terms of altering the crystalline structure of this polymer. That the addition of plasticizer decreases the degree of crystallinity is quite likely, since the action of a compatible plasticizer is as a solvent and any crystalline phases would tend to be less stable in the presence of solvent. It is dubious, however, in the light of this investigation whether this can be the major effect produced by the plasticizer, since any reduction in crystallinity would be expected to yield an increase in slope of the transition region. It would also be expected that the action of plasticizers in broadening the transition region would be unique to systems involving crystalline or semicrystalline polymers and that the behavior of completely amorphous polymers in the transition zone would be relatively unaffected by the addition of plasticizer apart from the lowering of the glass transition temperature.

In order to investigate this, the master curves were obtained for poly(vinyl chloride) plasticized with 16% of ethyl hexyl phosphate and for similarly plasticized polystyrene. These are shown in Figure 5. As may be observed, there is a marked decrease in the value of n from pure polystyrene to the plasticized composition as well as in the case of poly(vinyl chloride). This would indicate that the mechanism of plasticizing action is much more general and does not depend on the morphology of the polymer. Additional evidence for this view is given by the work of Carlson, Indictor, and Tobolsky.[19] For polystyrene plasticized with 16% dioctyl phthalate the value of n was 0.5 compared with a value of 0.8–1.0 for unplasticized polystyrene.[12] The value of n for similarly plasticized poly(methyl methacrylate) was 0.49, which is still lower than the average value of 0.55 for the parent polymer. Shen,[20] investigating the modulus–temperature behavior of lightly crosslinked polystyrene and poly(ethyl meth-

acrylate) preswollen by plasticizer, found that the slope s in the transition region was decreased by increase in plasticizer concentration.

Figure 5 also shows a more rapid decrease from the rubbery plateau to the flow region for plasticized polystyrene. This may be due to the lowering of the molecular weight average by addition of plasticizer. In order to obtain some quantitative information on this, the maximum relaxation times τ_m of polystyrene and plasticized polystyrene were calculated by using the relationship

$$\log 3G_r(t) = \log 3G_m - (t/2.303 \; \tau_m) \tag{4}$$

at the glass transition temperatures, i.e., 100 and 47.5°C., respectively. The values thus obtained were 5.43×10^9 sec. for polystyrene and 4.0×10^9 sec. for the plasticized material.

It has been shown[25] that for a given polymer τ_m should depend on $\bar{M}_w$ to the power 3.4. For the present case

$$\tau_m \; _{\text{unplast.}}/\tau_m \; _{\text{plast.}} = 1.36$$

and

$$\bar{M}_w^{3.4} \; _{\text{unplast.}}/\bar{M}_w \; _{\text{plast.}} = 1.81$$

These results, while approximate, indicate that the behavior of plasticized polystyrene in the rubbery flow region may be semiquantitatively accounted for by the change in molecular weight on plasticization.

Temperature Dependence of Characteristic Relaxation Times

Currently the most satisfactory way to express the temperature dependence of the viscoelastic behavior is embodied in the equation proposed by Williams, Landel, and Ferry[21] based on the concept of a constant fractional free volume at the glass transition temperature. This has been modified by Catsiff and Tobolsky[22] to

$$\log K(T)/K(T_d) = -16.14 \; (T - T_d)/(56 + T - T_d) \tag{5}$$

where T_d is a characteristic temperature close to T_i. The composite results of this investigation plotted as $\log K(T)/K(T_i)$ versus $T - T_i$ are shown in Figure 8. Equation (5) is also plotted as the dotted line. It can be seen that above T_i the results obtained for all the systems studied are consistent with this equation although, in general, the experimental scatter is high. Below T_i the experimental results yield values of $\log K(T)/K(T_i)$ which are much smaller than those expected from the above equation. This is understandable since the variation of free volume with temperature is not likely to be the same above and below the inflection or glass transition temperature. It is felt that the low values reported[19] for the gradient of the WLF equation at T_i were obtained by taking into account values lying above and below T_i and do not, therefore, affect the applicability of eq. (4) which should yield a slope of 0.288 at T_i.

The above evidence would indicate that, while the addition of plasticizer reduces the inflection and glass transition temperatures of poly(vinyl chloride) it does not substantially alter the microcrystalline structure.
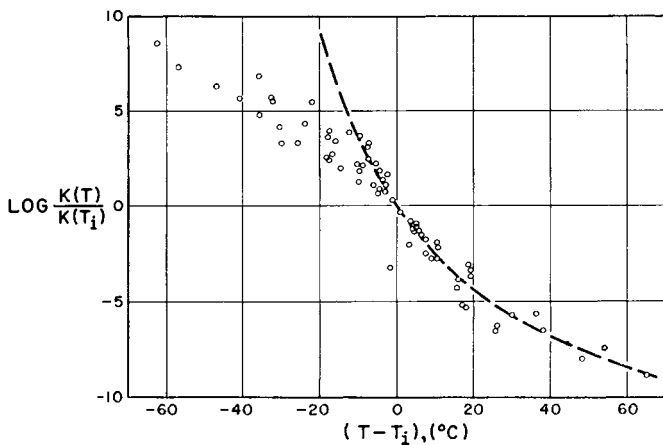
Fig. 8. Plot of temperature dependence of characteristic relaxation times for poly(vinyl chloride) compositions.
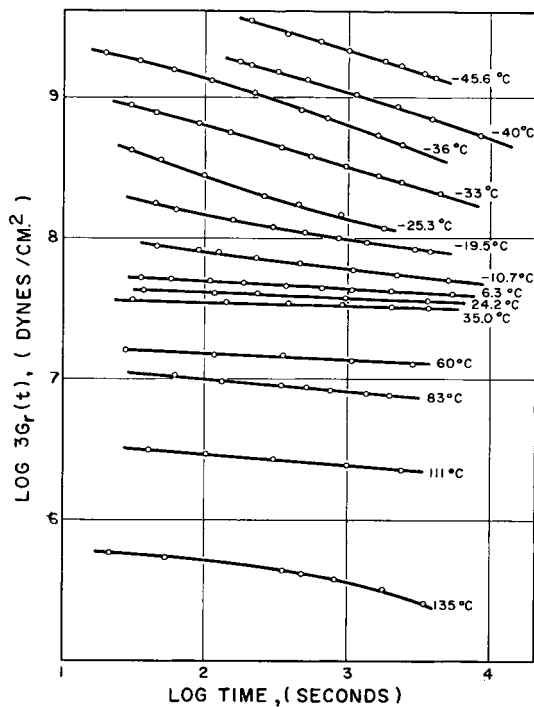
Fig. 9. Variation of modulus with time for plasticized poly(vinyl chloride) (44%) at high temperature.

Such an effect could account for the valuable properties of poly(vinyl chloride) on the practical level. That is, the material may be rendered flexible at room temperature by the addition of a proportion of plasticizer without sacrificing the high creep recovery properties. With a similar polystyrene composition the reduction of the glass transition temperature would be accompanied by a lowering of the temperature at which rubbery flow causing permanent deformation would occur. For a similar effect to occur in poly(vinyl chloride), plasticizer would have to, in addition, lower the melting points of the crystallites rendering the material amorphous. The work of Anagnostopoulos et al.[17] shows that for a volume fraction of 0.97 diluent the melting point was reduced from 174 to 116°C. This would indicate that for the plasticizer concentrations employed in the present study the temperatures at which flow could occur in the time of measurement would be well above this temperature. A series of measurements of stress relaxation was made for the most highly plasticized of the samples in an attempt to detect complete melting of the crystallites by observing a rubbery flow region. The results are shown in Figure 9. These indicate that rubbery flow, even for a highly plasticized sample of poly(vinyl chloride), commences only around 135°C. This tends to substantiate that plasticizer only acts as an impurity to depress the melting point of the crystallites and that the magnitude of the effect is such that, at temperatures even above the glass transition, no appreciable decrease in crystallinity is produced.

In conclusion, it may be suggested that the present investigation lends confirmation to the idea that poly(vinyl chloride) has a structure which is semicrystalline in nature, the crystallites being small enough to act as crosslinks. The action of plasticizers on poly(vinyl chloride) is similar to their effect on completely amorphous polymers, but the crystallites remain stable under the action of plasticizer. These two facts combined form the basis for the wide range of usefulness of poly(vinyl chloride).

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Résumé

On a déterminé les courbes maîtresses de relaxation de la tension du chlorure de polyvinyle plastifié à divers degrés par le phthalate de dioctyle [di(2 éthyl-hexyl)-phthalate]. On discute ces résultats en fonction de la concentration en agent plastifiant et de la structure du polymère. On rapporte également des courbes module-température calculées à partir des courbes de relaxation. On compare les résultats obtenus pour le chlorure de polyvinyle plastifié aux résultats obtenus pour le polystyrène plastifié. On discute des propriétés commerciales intéressantes du chlorure de polyvinyle à la lumière de ces données sur la structure du polymère et sur l'action de l'agent plastifiant.

Zusammenfassung

Die verallgemeinerten Spannungsrelaxationskurven mehrerer mit verschiedenen Mengen Dioctylphthalat [Di-(2-äthylhexyl-)phthalat] weichgemachten Polyvinyl-chloridproben werden beschrieben und in bezug auf Weichmacherkonzentration und Polymerstruktur diskutiert. Ausserdem werden die aus den experimentellen Daten ermittelten Modul-Temperaturkurven angegeben. Es werden Vergleiche zwischen weichgemachten Polyvinylchlorid- und Polystyrolproben angestellt. Schliesslich wird die technische Brauchbarkeit von Polyvinylchlorid auf der Grundlage der experimentellen Daten über Polymerstruktur und Weichmacherwirkung diskutiert.