

Rates of Property Change in Plasticized Filled PVC Compounds

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Synopsis

Rheological and mechanical properties of polyvinyl chloride (PVC) compounds vary with the polymer entanglement state at the time of testing. Controlled shearing episodes and thermal histories applied to the compounds produce major property variations. These then relax toward steady-state values at rates which are consistent with diffusion-controlled processes, presumably connected with the development of steady-states in entanglement couplings. Activation energies of 4-7 kcal/mol apply to the proposed re-entanglement processes. Rates of property variation can be altered by the addition of fillers to the compounds, the interactions between polymer and filler being an important factor in this regard. CaCO₃ samples with strong affinity for the PVC retard the rate of property variations (i.e., the filler tends to stabilize non-steady-state entanglement couplings). Fillers, surface treated so as not to interact strongly with the polymer, produce lesser effects on relaxation rates. The data indicate the feasibility of controlling both the sensitivity of polymer properties to processing variables, and the rates of property change associated with the attainment of steady-state polymer entanglement morphologies.

INTRODUCTION

Long relaxation times in polymers can be related to time-dependent adjustments in the entanglement network structure of the polymer following some perturbation of that structure. In several recent publications¹⁻⁴ it has been noted that the thermal history and particularly the shear history of a polymer may influence the processability of the material and its mechanical properties. When these properties are determined with the polymer network structure in a non equilibrium state then time-dependent processing and property changes will be observed as equilibrium entanglement morphologies are attained. As has been suggested recently,³⁻⁴ it appears that diffusion-controlled mechanisms are involved in the attainment of entanglement equilibria.

The susceptibility, specifically, of polyvinyl chloride (PVC) compounds to the effects of changes in entanglement states brought on by shearing or by solution-precipitation treatments has been reported earlier.³ In this paper we examine the behavior of filled, mildly plasticized PVC compounds, variously surface-treated fillers having been introduced in an attempt to control the kinetics of property change following network modification.

The premise involved is that specific interactions at polymer-filler contacts may affect the segmental mobility of the polymer, and therefore influence the

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kinetics of re-entanglement in modified polymers. This portion of our studies was intended to test the stated premise and thus also to help establish the mechanisms of time-dependent property changes in shear or solution-modified polymers.

EXPERIMENTAL

A standard PVC formulation was used throughout this work. It was based on K-65 PVC resin supplied by Esso Chemical (Canada) Ltd. and had the following composition:

PVC	100 phr
DIOP Diisooctylphthalate	12.5 phr
Tribase stabilizer3 phr

The filler selected was CaCO_3 . Two surface-treated versions were involved:

- (CaCO_3)-I B.E.T. surface area of $5.5 \text{ m}^2 \text{ g}$
- (CaCO_3)-II B.E.T. surface area of $6.4 \text{ m}^2 \text{ g}$

Filled compounds used versions I and II at 2 and 10 vol% loadings.

Test compounds were prepared by first blending components in a Brabender mixer at 120 C and 40 rpm to constant torque, the procedure generally lasting about 6 min. This preliminary step ensured good plasticizer uptake and uniform dispersion of components, without seriously altering the entanglement states of the polymer samples involved in the compound. Compounds were made with the PVC as received, and in modified entanglement state, represented by recovering the polymer from 0.2% solutions in tetrahydrofuran (THF) by the addition of water.³ The solution-modified polymer was vacuum dried (72 h 50°C); infrared data and differential scanning calorimetric (DSC) scans were determined to ensure removal of solvent residues. Blended samples were then fused by compression molding at 190°C. Molded plates were shock-cooled to room temperature and tested in stress-strain (Instron Table model tester 2.0 cm/min jaw separation) and for dynamic mechanical responses using a Rheovibron at 11 Hz. Repeat evaluations were made on samples annealed at 40, 60, 80, and 100°C for periods up to 100 hours. The isothermal annealing periods were intended to indicate rates of property change on either side of the glass transition temperature; the latter was shown to lie in the vicinity of 80°C for the slightly plasticized control compound (see below). All reported data are averages of at least 3, and in most cases, 5 separate determinations.

The quality of interactions at polymer-filler contacts was evaluated from an application of inverse gas chromatography (IGC). The principle involved and details of experimentation have been discussed in recent publications.^{5,6} Briefly, specific retention volumes, V_g° , obtained for polymer and fillers as stationary phases, and using vapor probes selected for their acid and base character, permit the evaluation of an acid-base interaction parameter, Ω . This is defined⁶ as

$$\Omega = 1 - (V_g^\circ)_b / (V_g^\circ)_a$$

TABLE I
Interaction Parameters for Compound Materials

	PVC	CaCO ₃ -I	CaCO ₃ -II
$V_g^\circ(30^\circ\text{C})$			
<i>n</i> -butanol	21.3	61.4	52.0
<i>n</i> -bu.amine	64.5	36.8	46.4
$\Omega (\pm 0.5)$	-2.03	0.67	0.12

for stationary phases which are acidic, and

$$\Omega = (V_g^\circ)_a / (V_g^\circ)_b - 1$$

for stationary phases which are basic. The $(V_g^\circ)_a$ and $(V_g^\circ)_b$ designate retention volumes for acidic and basic vapors, respectively. Since for an acidic substrate $(V_g^\circ)_b > (V_g^\circ)_a$, it follows that $\Omega < 0$. Conversely, $\Omega > 0$ for a basic solid, while nonpolar or amphipatic substrates will report $\Omega \approx 0$.

As in previous evaluations of acid-base interactions,^{5,6} *n*-butyl alcohol and *n*-butyl amine were the acid and base vapor probes. All other experimental procedures also followed those described in the earlier communications. The IGC characteristics are summarized in Table I.

The Ω values show PVC to behave as a Lewis acid, while CaCO₃-I has distinctly basic properties. CaCO₃-II, with a very slightly positive Ω value, may be regarded as being close to "neutrality" on the present scale of acid-base interaction potentials. Much stronger polymer-filler interaction would be expected to occur at contacts between PVC and CaCO₃-I than between the polymer and CaCO₃-II.

RESULTS AND DISCUSSION

The stress-strain and dynamic mechanical properties of the test specimens are summarized in Table II. Stress-strain results are represented by the tensile modulus and elongation at rupture, the dynamic mechanical properties by the storage modulus at a reference temperature of 0°C and by the apparent T_g , read with a precision of $\pm 1^\circ\text{C}$ from the peak in representations of $\tan \delta$ vs. T . The results for unmodified, control PVC compound, and for the compound using PVC recovered from THF solution are very similar to those reported earlier.³ The use of solution-modified polymer leads to marked reductions in moduli and ductility, and to a significant decrease in the apparent transition temperature. Apparently the solution-precipitation step is effective in modifying the network morphology in compounds using this version of the polymer. The solution-modified polymer was used as host for all filled PVC compounds. The data in Table II show that both fillers influence compound properties, but the suggested strength of interfacial contacts between PVC and CaCO₃-I leads to a marked differentiation between compounds using fillers I and II. Perhaps most obvious is the effect on compound ductility; at 2 vol% of filler I this is actually increased over that of the pertinent control, while the use of II leads to a further reduction. Although compounds with 10 vol% filler have reduced ductility compared with the control, the effect is again far more

TABLE II
 Mechanical Properties of PVC Compounds

Property	Tensile-modulus (GPa)	Elongation @ rupture (%)	G' (GPa)	T_g^a (°C)
No. Material				
1. Control. Comp'd.	2.02	61	23.0	79
2. Unfiled:	1.85	22	13.0	66
Soln. mod. PVC				
3. 2 + 2 vol % CaCO ₃ -I	3.67	42	16.9	72
4. 2 + 10% CaCO ₃ -I	3.93	13	20.4	74
5. 2 + 2% CaCO ₃ -II	2.88	12	13.3	61
6. 2 + 10% CaCO ₃ -II	3.04	3.5	15.2	67

^aFrom maxima in $\tan \delta$ vs. T .

severe when filler II is involved. Tensile and storage moduli, as well as $\tan \delta$ (i.e., T_g) report similar effects: Compound reinforcement by filler I is more successful than when version II is involved; in addition, the T_g is decreased when filler II is used, but increases slightly in compounds with filler I. Assuming that stronger wetting and adhesive bonding occurs in PVC-I than in PVC-II, the data in Table II give evidence of the important contribution made by interfacial forces to the mechanical properties of these compounds.

Annealing experiments at temperatures stated in the preceding section were used to follow the evolution of properties in systems using the solution-modified polymer. Initial, control experiments conducted at 60°C annealing temperature permitted a comparison to be made with rates of equilibrium attainment in compounds using the PVC as received. The elongation (ϵ) and storage modulus (G') illustrate the response of the unmodified polymer to annealing, as shown in Figure 1. Though small, the changes are significant and indicate that these compounds are not in equilibrium states as prepared for testing. Data of the type given in Figure 1 were used to calculate difference parameters

$$\Delta P = P_c - P_m$$

where P_c is the property of compounds with PVC as received, and P_m is the corresponding property when solution-modified PVC is used. The results of such analysis, again for 60°C annealing, are illustrated in Figures 2 and 3, for elongation and T_g , respectively. The effects of 2 vol% loadings of fillers I and II are represented in these figures.

Several consistent features may be noted in Figures 2 and 3. Over substantial ranges of annealing time, the experimental data for property change are linear in $t_{1/2}$, suggesting that (Fickian) segmental diffusion processes are involved in property evolution. Furthermore, in the unfilled compounds, very significant differences are noted in the times taken to attain equilibrium values of ϵ_r and T_g , the former requiring about 50 h at 60°C, the latter only

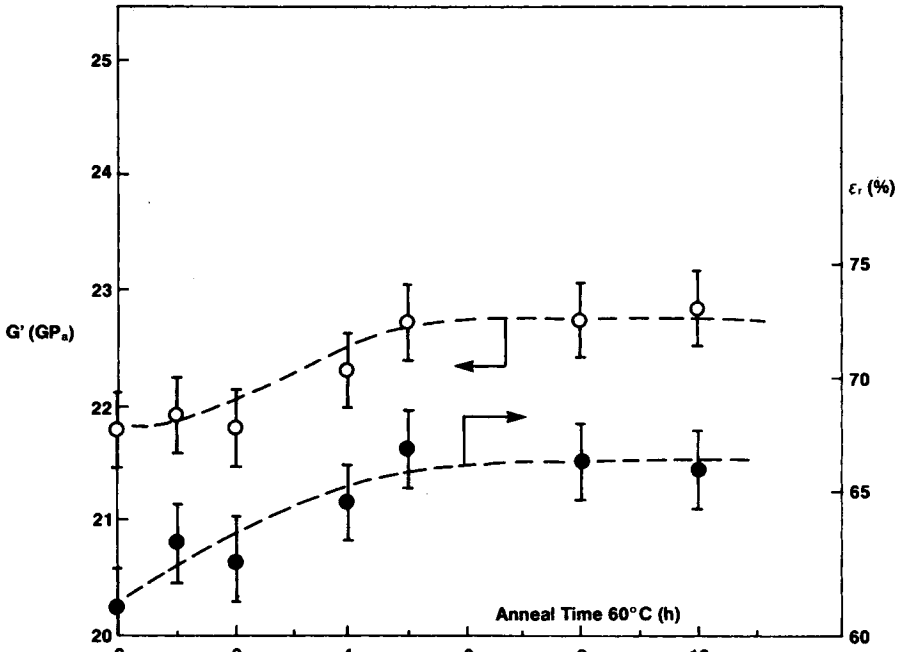


Fig. 1. Response of control polymer properties to 60°C annealing; G' measured at 0°C.

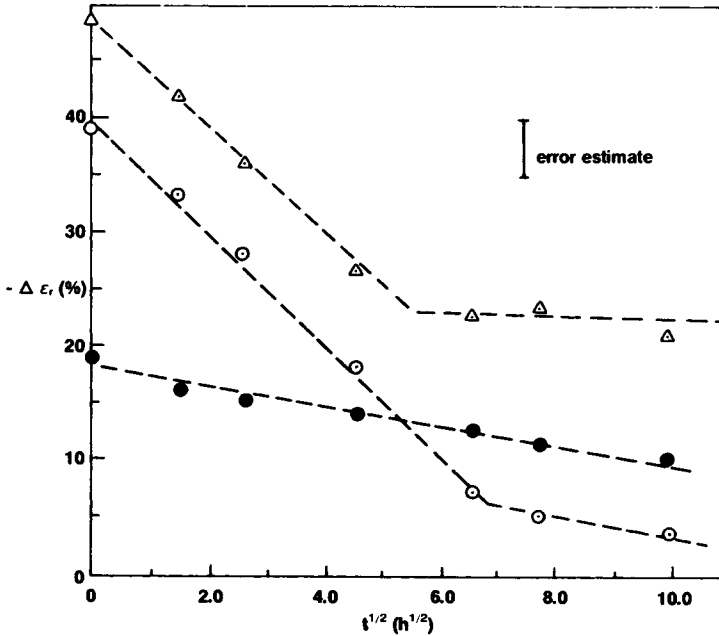


Fig. 2. Effect of 60°C annealing on loss of elongation at rupture: (○) unfilled PVC, using solution-modified polymer; (●) 2 vol% CaCO_3 -I; (Δ) 2 vol% CaCO_3 -II.

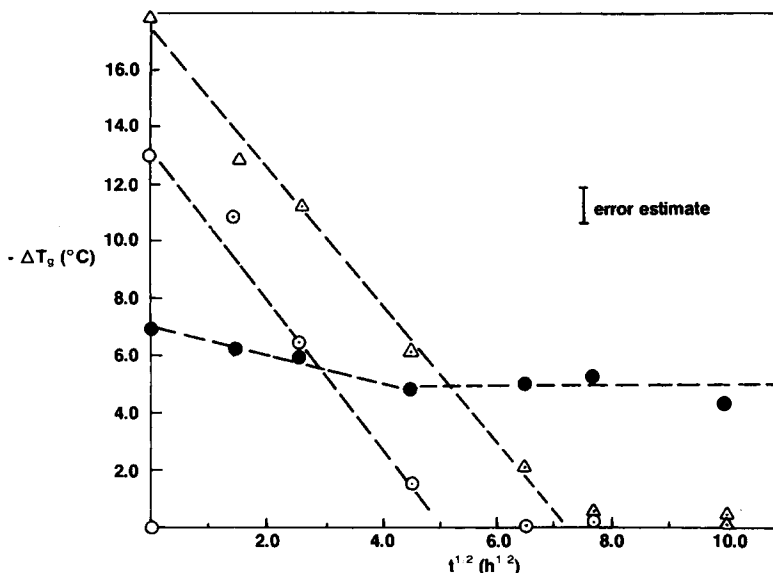


Fig. 3. Effect of 60°C annealing on changes in T_g of PVC compounds: (○) unfilled PVC, using solution-modified polymer; (●) 2 vol% CaCO₃-I; (△) 2 vol% CaCO₃-II.

about 25 h. Evidently different aspects of network morphology dominate these properties of the polymer solid. We suggest that ultimate mechanical properties, as represented by ϵ_r , depend strongly on longer-range, network-stabilizing entanglements, for example those capable of interconnecting elastically deformable domains which may have been isolated by previous shear of solution histories. On the other hand, T_g and viscous properties of the polymer may depend principally on entanglements at the segmental level, with a corresponding reduced relaxation time.

Finally, the effects of fillers I and II on annealing processes are strongly differentiated. CaCO₃-II which interacts weakly with the polymer, increases the overall property modification, but has no apparent effect on the kinetics of re-entanglement, the linear portions in Figures 2 and 3 being parallel with those for unfilled, modified PVC. In contrast, use of CaCO₃-I, where stronger adhesion at polymer-filler contacts is indicated, tends to stabilize the solution-modified morphology over periods exceeding the limits of present studies.

Annealing experiments at the other temperatures, as specified earlier, permit a closer analysis of property re-establishment kinetics. The subject is illustrated in the two parts of Figure 4. Time-dependent changes in elongation for compounds with filler I are shown in Figure 4(A), those for compounds with filler II are illustrated in Figure 4(B) in terms of T_g . Similar patterns of behavior were noted for tensile and storage moduli. The diffusion-dependent rates of property re-establishment are again indicated by the linear segments in representations where root-time is used as the abscissa. Annealing above the T_g shows trends to the establishment of steady states, these being much less affected by the presence of filler II than of filler I. For example, as in

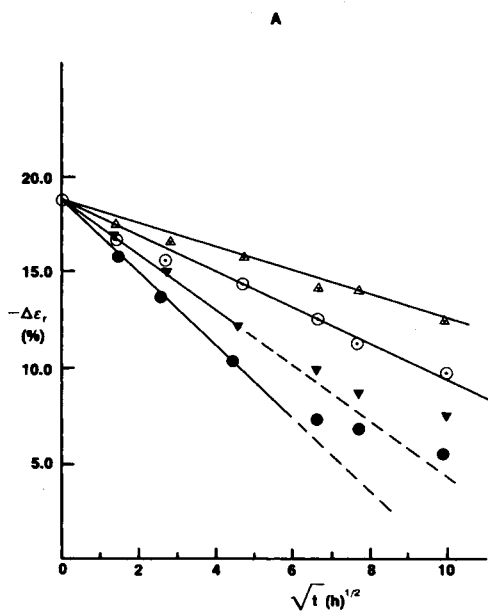


Fig. 4(a). Illustrating response of elongation at rupture to annealing temperatures for compounds with 2 vol% filler I: (Δ) 40°C; (○) 60°C; (▼) 80°C; (●) 100°C.

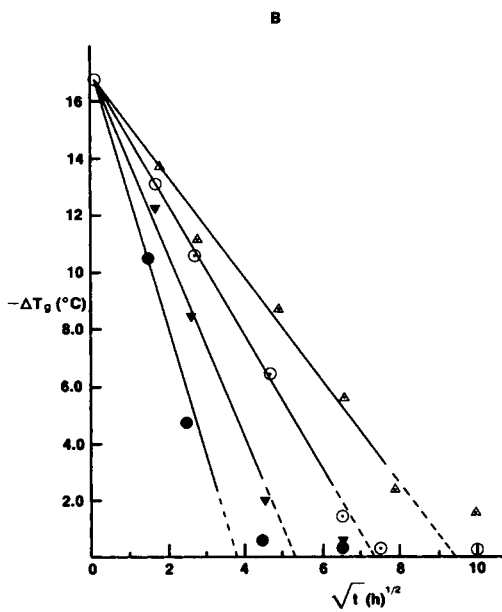


Fig. 4(b). Illustrating response of T_g to annealing temperature for compounds with 2 vol% filler II: (Δ) 40°C; (○) 60°C; (▼) 80°C; (●) 100°C.

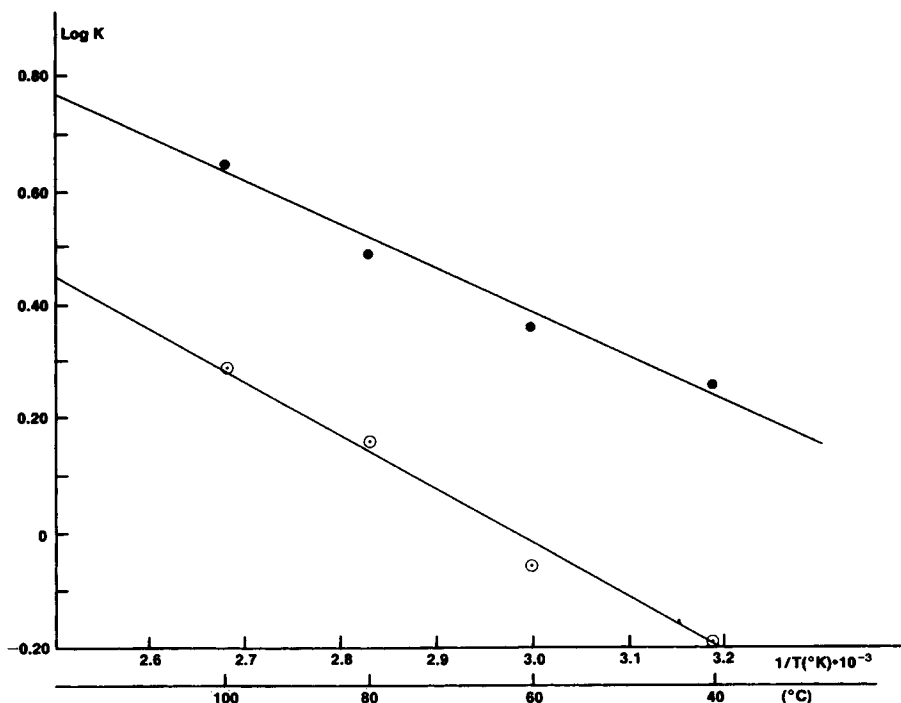


Fig. 5. Illustration: Arrhenius-type relationships for annealing responses of filled PVC compounds: (●) T_g variation, filler II; (○) Elongation variation, filler I.

Figure 4(B), the T_g of compounds with filler II attains the value for the host polymer in about 16 h at 100°C and some 30 h at 80°C; apparently so little contact persists at polymer-filler interfaces, that the polymer behaves as though (at low filler volume) it were unperturbed by the filler. In Figure 4(A), the experimental time was inadequate for the establishment of steady states and, as noted already, the trend is to modified properties, due to strong polymer-filler interaction.

The slopes of linear segments in graphs such as those shown in Figure 4 were used to evaluate kinetics of property change. These slopes, termed K , were then plotted against $1/T$, producing Arrhenius-type functions, as shown in Figure 5. Somewhat surprisingly, the linear fit to experimental points included the 100°C annealing sequence. Since this temperature exceeds the T_g , a discontinuity in rates of property change might have been expected. Annealing at additional higher temperatures will be needed to clarify this point.

The activation energies calculated from the constructions illustrated in Figure 5, fell in a narrow range of 4–6.5 kcal mol. These values are in general agreement with expectations for diffusion-controlled processes in thermoplastic polymers.⁷ The approximate equality of activation energies for compounds with 2% fillers I and II is also noteworthy. It suggests that relatively short segments of the polymer chain are adsorbed on the filler surface. This leads to a decrease in the absolute mobility of the macromolecule, as indicated by substantial differences in the re-entanglement rates [Figs. 4(A), (B)], but leaves unaffected the energy requirements for re-entangling the free segments

of the polymer chain. The implied mechanism is similar to that proposed recently for filled silicon rubbers by Cohen-Addad and co-workers.⁸ Of course, an increase in the strength of acid-base coupling beyond that represented by filler I, (in this case requiring a filler with a higher Ω value than CaCO_3 -I), should anchor the polymer more closely to the particle surface leading, finally, to an inhibition of segmental diffusion. In this manner it may be possible to stabilize network structures in whatever states may be produced by processing steps designed specifically to control selected properties of polymer compounds.

This work was supported by a P.R.A.I. grant of the Natural Sciences and Engineering Research Council, Canada. The active support of an industrial advisory group is gratefully acknowledged.

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Received July 18, 1986

Accepted October 14, 1986