

## Effect of Stabilizers on the Melt Rheology of Poly(vinyl chloride)

L. B. WEISFELD, G. A. THACKER, and L. GIAMUNDO

Advance Division, Carlisle Chemical Works, Inc., New Brunswick, N. J. 08903

*Rheological studies using the Brabender plastograph show that the magnitude of the torque plateau generated by molten, unplasticized poly(vinyl chloride) depends greatly on the nature of the metal or organometallic stabilizer incorporated. These effects are related to the extrusion rates and dynamic processing liability of the resin compound. It is proposed that the apparent increase in viscosity is caused by the propensity of the metal atom of the stabilizer to satisfy its vacant d-orbital requirements with the p-electrons of the pendent substituents on the polymer chain, thereby setting up secondary crosslink structures and increasing the dynamic liability of the compound. Low melt viscosities engendered by organotin mercaptides are explained by intramolecular d $\pi$ -p $\pi$  orbital fulfillment.*

Since a wide variety of thermoplastic materials are fairly stable at processing temperatures, the incorporation into them of low molecular weight adjuvants, notably stabilizers and antioxidants, is almost superfluous. No one will say that such adjuvants are unnecessary, but in many cases the benefits are related mainly to end use and the retardation of aging effects. Poly(vinyl chloride) (PVC), however, is perhaps the most liable of the commercial thermoplastics. Processing of PVC is hardly possible without using stabilizers, and most practical innovations in PVC applications have been foreshadowed by advances in stabilizer technology.

In the early history of PVC, application was confined almost entirely to highly plasticized and flexible compositions, and the thermal processing liability of such formulations was practically the only question. Minimal mechanical shear work was applied to the polymer itself. Concomitant with the growth of the industry was the discovery that certain metal soaps

and combinations effectively retarded thermal degradation during processing. It was sufficient, for the most part, to determine the efficacy of a stabilizer system for any particular PVC formulation by a relatively simple "oven test," whereby PVC films were incubated in a circulating air oven for varying periods of time, and the rate of color development was noted.

With the discovery of the organotin mercaptide stabilizers came the realization that much more could be demanded of the processing latitude for PVC. Plasticizer levels dropped, and rigorous extrusion techniques became practical, leading eventually to the production of clear and rigid PVC articles. Today, the most interesting and rapidly growing area of PVC application technology is in rigid products (bottles, pipes, building materials). Much more is demanded of a stabilizer than its simple thermal response. The "oven tests" are no longer sufficient and, indeed, scarcely correlate with the phenomena obtained in the extruder. A critical distinction exists between the "static" and "dynamic" thermal liability of PVC.

It is not the purpose of this paper to review or expound on the well-documented stabilization mechanisms for PVC. Nor will we consider the other well known auxiliaries to PVC stabilization such as phosphites, epoxies, and hindered phenols. Rather, attention will be paid to only the primary metallic and organometallic stabilizers, the principle elements illustrated in Table I. The metal soap derivatives of the Group

**Table I. Elements of Metallic (or Organometallic) Stabilizers of Interest in Stabilizing Poly(vinyl chloride)**

Periodic Arrangement of Stabilizer Elements

<i>Group</i>			
<i>I</i>	<i>II</i>	<i>IV</i>	<i>V</i>
(Na)	Mg	(Ge)	
K	Ca		
	— Zn		
	Sr	Sn	Sb
	Ba	Pb	(Bi)
	— Cd		

II elements invariably are not used singly, but in Subgroup A-B couples. Aside from lead compounds, the elements currently used in most applications are barium, cadmium, calcium, zinc, and tin—*e.g.*, the calcium–zinc soap systems for nontoxic (food contact) applications, the general purpose barium–cadmium soap stabilizers, and the organotin stabilizers. The objective of this paper is to consider the rheological consequences of

using these materials in rigid PVC and to provide a possible explanation for this behavior.

### Experimental

The Brabender plastograph was used for these investigations with a 120-mm. chamber, roller heads, oil heated, and ram charged. A typical plastograph curve, with its important characteristics, is illustrated in Figure 1. The time to decomposition of rigid PVC is usually noted by an upward inflection at the end of the curve, where crosslinking ostensibly occurs. This inflection is coincident with the evolution of HCl, detected by Congo Red paper. More important for current considerations, the minimum torque plateau preceding decomposition provides an estimate of the effect of the stabilizer component on the melt viscosity of the compound, all other compound factors being equivalent.

Two types of resin were investigated: PVC homopolymer (Opalon 630) and copolymer (Diamond CR-80). The stabilizer systems used are indicated in Table II. The organotin series of stabilizers proceeds from

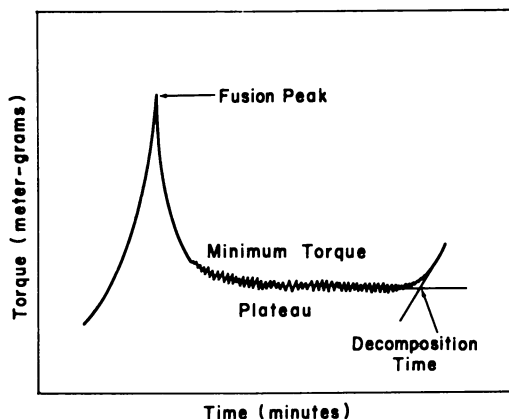


Figure 1. Typical Brabender plastograph curve

Table II. Stabilizers Used in Dynamic Stability Studies

Stabilizer	Identity
$\text{Bu}_2\text{Sn}(\text{SCH}_2\text{COOR})_2$	Dibutyltin bis(isooctyl acetomercaptide)
$\text{Bu}_2\text{Sn}(\text{SR})_2$	Dibutyltin bis(lauryl mercaptide)
$\text{Bu}_2\text{Sn}(\text{SCH}_2\text{CH}_2\text{COO})$	Dibutyltin mercaptopropionate
$\text{Bu}_2\text{Sn}(\text{OCOCH}=\text{CHCOOR})_2$	Dibutyltin bis(isooctyl maleate)
BC-1	14% Ba, 7% Cd carboxylates
BC-2	7% Ba, 11% Cd carboxylates
CZ-1	1% Ca, 1% Zn carboxylates
CZ-2	1% Ca, 2% Zn carboxylates

those with only tin-carbon and tin-sulfur bonds, through one with tin-carbon, tin-sulfur and tin-oxygen bonds, to finally a tin-carbon, all tin-oxygen bond species. Formulated compounds were "dry blended" in a laboratory Henschel mixer. In addition to the stabilizers and amounts

**Table III. Plastograph Results for PVC Homopolymer with Various Stabilizers<sup>a</sup>**

<i>Stabilizer</i>	<i>Concentration, % per 100 resin</i>	<i>Minimum Torque, meter- grams</i>	<i>Decompo- sition, minutes</i>	<i>Stock Temper- ature, °F.</i>
Bu <sub>2</sub> Sn(SCH <sub>2</sub> COOR) <sub>2</sub>	2.0	2350	18.8	395
Bu <sub>2</sub> Sn(SR) <sub>2</sub>	2.0	2200	12.6	400
Bu <sub>2</sub> Sn(SCH <sub>2</sub> CH <sub>2</sub> COO)	1.0	2400	9.9	400
Bu <sub>2</sub> Sn(OCOCH=CHCOOR) <sub>2</sub>	2.1	2650	4.8	405
BC-1	2.0	2600	7.5	390
BC-2	2.0	3100	17.4	395
CZ-1	2.0	2800	6.3	390
CZ-2	2.0	2700	5.0	390
None	—	2750	4.5	410

<sup>a</sup> Resin, Opalon 630, 100.0 p.h.r., with 1.0 p.h.r. epoxidized soya oil and 0.25 p.h.r. glyceryl monostearate. Sheared at 175°C., 40 r.p.m.

**Table IV. Plastograph Results for PVC Copolymer with Various Stabilizers<sup>a</sup>**

<i>Stabilizer</i>	<i>Concentration, % per 100 resin</i>	<i>Minimum Torque, meter- grams</i>	<i>Decompo- sition, minutes</i>	<i>Stock Temper- ature, °F.</i>
Bu <sub>2</sub> Sn(SCH <sub>2</sub> COOR) <sub>2</sub>	2.0	420	17.5	375
Bu <sub>2</sub> Sn(SR) <sub>2</sub>	2.0	500	14.6	375
Bu <sub>2</sub> Sn(SCH <sub>2</sub> CH <sub>2</sub> COO)	2.0	590	10.5	375
Bu <sub>2</sub> Sn(OCOCH=CHCOOR) <sub>2</sub>	2.0	600	11.5	374
BC-1	3.0	610	7.7	370
BC-2	3.0	600	7.5	370
CZ-1	2.0	900	1.8	375
CZ-2	2.0	900	3.3	365
None	—	620	9.3	375

<sup>a</sup> Resin, Diamond CR-80, 100.0 p.h.r. Sheared at 180°C., 35 r.p.m.

noted in Table III, the homopolymer was compounded with 1.0 p.h.r. (per 100 parts of resin) of epoxidized soya oil and 0.25 p.h.r. glyceryl monostearate. No additional adjuvants were used with the copolymer resin. Sixty grams of each compound were rammed into the plastograph chamber, and those of the homopolymer were sheared at 175°C. jacket temperature and 40 r.p.m. Copolymer compounds were sheared at 180°C., 35 r.p.m. The results for homopolymer are shown in Table III and those for copolymer in Table IV.

### Discussion

The lowest melt viscosities are provided by the organotin mercaptides, as are the longest stabilization periods. As tin-oxygen bonds replace the tin-sulfur bonds, the melt viscosities increase and the stabilization times diminish. These phenomena cannot be explained on the basis of simple plasticization or "internal lubricity" since no structural correlations are apparent. For example, the dibutyltin bis(isooctyl maleate) and dibutyltin bis(isooctyl thioglycolate) are liquids of approximately the same viscosity and molecular weight, and yet they provide opposing melt viscosity behavior. Further, the magnitude of increase in melt viscosity for homopolymer between these two stabilizers (13%) is smaller than that for copolymer (43%). The barium-cadmium stabilizers and the calcium-zinc system also provide high melt viscosities, for the most part exceeding that for the organotin carboxylate.

A probable explanation for these effects resides in a recognition of the vacant *d*-orbital requirements of the metal (organometal) stabilizers. The increase in melt viscosity may be the product of an intermolecular chain association through the vacant *d*-orbitals of the organotin carboxylates, which have a hexacoordinate aptitude, or those of the Group II metals, which have a tetracoordinate aptitude for the most part. Thus, the vacant orbital requirements are satisfied through coordination with the *p*-electrons of pendent substituents on the polymer chain, setting up secondary crosslinks in the polymer network, as shown in Figure 2. The

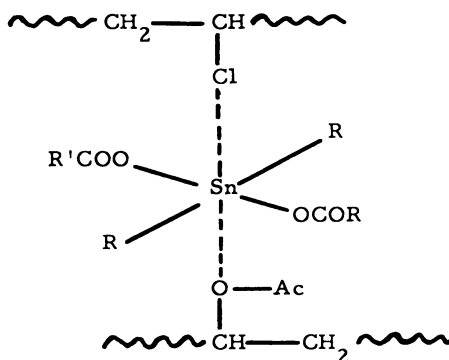


Figure 2. Probable configuration of a secondary crosslink in a PVC-PVAc melt

situation would probably be further aggravated in copolymer (vinyl acetate) systems because of the greater basicity of oxygen over chlorine. Such a configuration as shown in Figure 2 has been considered previously in explaining the mechanism of stabilization afforded by organotin com-

pounds and other metal salts (2). However, it was invoked without considering the consequences of dynamic liability.

Attention is drawn to the feature of 17.4 minutes of apparent stabilization provided by BC-2 in homopolymer (Table III). This is inordinately long and demonstrates that torque plateaus under consideration do not necessarily correspond with stabilization times. For that matter, BC-2 is unique in that it contains an organic auxiliary stabilizer which, although it apparently increases the "decomposition" time, does not otherwise diminish the polymer bonding aptitudes of the metal-containing stabilizer.

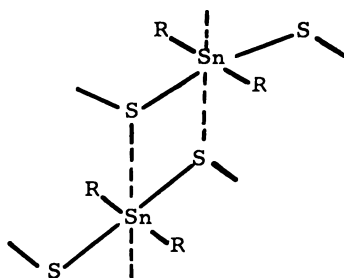


Figure 3. Possible route to orbital requirement satisfaction within the organotin mercaptide series

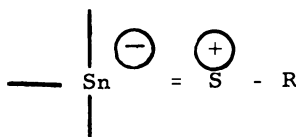
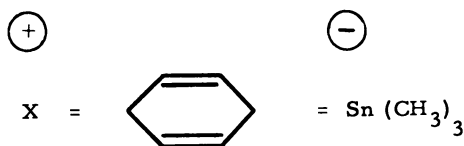


Figure 4. Representation  $d_{\pi}-p_{\pi}$  overlap between tin and sulfur

With the organotin mercaptides, the lowest melt viscosities are manifest. This can be explained by the ability of sulfur to expand its octet, or more correctly, by the ability of sulfur pi electrons to overlap the vacant tin  $d$ -orbitals. Oxygen has a much lower aptitude for such. One possible polymeric configuration for organotin mercaptides is shown in Figure 3. In lieu of this, it is more probable that significant  $d_{\pi}-p_{\pi}$  bonding occurs intramolecularly between tin and sulfur (Figure 4). Such has been suggested for certain trimethylphenyltin derivatives (3), where electric dipole measurements indicate that structures such as that in Figure 5 contribute to the ground state of molecules wherein strongly



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Figure 5. Electric dipole representation of trimethylphenyltin derivative

electron-releasing substituents are attached para to the  $\text{Sn}(\text{CH}_3)_3$  group. It has even been suggested that double bond character between  $\text{Sn}-\text{C}$  or  $\text{Sn}-\text{halogen}$  exists in the series  $(\text{CH}_3)_n\text{SnX}_{4-n}$  where X is Cl, Br, and I through PMR spectra and electric moment studies (4). The existence of such double bond character between tin and sulfur would obviate the necessity of using pendent pi-electron rich substituents on polymer chains for satisfying orbital requirements. That such requirements are fulfilled by sulfur next to tin is consistent with the foregoing observations.

The factors which cause an increase in melt viscosity of molten, unplasticized PVC are also responsible for the gelation of solutions of homo- and/or copolymer (1). For that matter, an analogous explanation is invoked, and it has been shown that displacement of simple ligands on the metal soaps by chelating types of ligands—i.e., those which possess pi-electron rich substituents adjacent to the principal point of attachment, will reverse gelation.

In summary, care must be exercised in choosing stabilizers for rigid PVC extrusion, and attention must be paid to the effect of such a stabilizer on the melt viscosity of the resin. By using a bonding type of stabilizer, not only may the melt viscosity be increased beyond practical extrusion rates, but the dynamic liability of compound is increased. Magnifying these effects are increased extruder residence time and a curtailment of regrind possibilities. For all these reasons and the foregoing considerations, the organotin mercaptides are, today, the most versatile and useful stabilizers for rigid PVC processing.

### Literature Cited

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