Zinc Maleate and Zinc Anthranilate as Thermal Stabilizers for PVC

ERNESTO URETA, MARÍA ELENA CANTÚ

División de Estudios Superiores, Facultad de Ciencias Químicas, Unversidad Autónoma de Nuevo León, Monterrey, N.L. México

Received 26 May 1999; accepted 10 September 1999

ABSTRACT: The results of the evaluation of zinc maleate and zinc anthranilate as thermal stabilizers for poly(vinyl chloride) (PVC) are reported in this article. Calcium stearate, diphenyl isodecyl phosphite, and epoxidized soya oil were used as costabilizers. Both zinc compounds showed good stabilizing performance in static and dynamic tests, particularly at low concentrations. The best results were obtained with zinc anthranilate. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2603–2605, 2000

Key words: zinc maleate; zinc anthranilate; PVC degradation; thermal stabilizers

INTRODUCTION

Poly(vinyl chloride) (PVC) is degraded by heat and shear during processing with the evolution of HCl. When HCl is eliminated from the chains, they develop sequences of conjugated double bonds that give several colorations to the polymer. The color changes from white to yellow, brown, and, finally, black, while the properties of the material deteriorate.[1–3] At the final stages of the degradation, crosslinking of the chains occurs.

The thermal instability of PVC is attributed to the presence of allylic and tertiary chlorine atoms, which are much more reactive than are secondary chlorine atoms.[4–6] It has also been demonstrated that HCl accelerates PVC degradation.[7]

The problem can be solved by the use of thermal stabilizers that must perform at least two basic functions: substitute stable groups for allylic and tertiary chlorine atoms and neutralize HCl. For this purpose, organometallic compounds are used. The best are based on tin, and, also, lead and barium–cadmium stabilizers are effective, but due to their toxicity, in some cases, they are substituted by calcium–zinc and barium–zinc stabilizers.[8]

EXPERIMENTAL

Materials

The Poly(vinyl chloride) (PVC) used in our experiments was a suspension homopolymer with $K = 66$. Zinc maleate was synthesized in the following way: dihydrated zinc acetate, 21.9 g (0.1 mol), was dissolved in 50 mL water and added to a solution of maleic anhydride (9.8 g, 0.1 mol in 50 mL water). The precipitate was filtered, washed with water, and dried at 100°C. Zinc anthranilate was prepared as follows: Zinc acetate, 0.1 mol, dissolved in 50 mL water, was mixed with 0.1 mol (13.7 g) of anthranilic acid also dissolved in 50 mL water. The precipitate was filtered, washed with water, and dried at 100°C.

Procedure

Several formulations, as indicated in Table I, were tested.

Correspondence to: E. Ureta.

Journal of Applied Polymer Science, Vol. 77, 2603–2605 (2000)

Table I Formulations of PVC with Additives

	●, ○	■, □	▲, △
PVC	100	100	100
Diphenyl isodecylphosphite	1	2	2
Epoxydized soya oil	2	2	3
Calcium–zinc stabilizer	4	4	4

Symbols refer to those in Figure 1.

The stabilizer was a mixture of calcium stearate with different amounts of zinc maleate or zinc anthranilate: 1, 2, 5, 10, and 20 wt %. Each formulation was evaluated by the Congo Red static test in which the time for the evolution of HCl is measured as the material is heated at 180°C in a test tube with a perforated cork from which hangs a piece of filter paper impregnated with a Congo Red indicator. The paper changes color from red to blue by contact with HCl. The best formulations were also tested by a dynamic method in a torque rheometer (Brabender Data-Processing Plasticorder PL 2000, with a roller-type mixer measuring head). The temperature was 180°C, and the rotor speed was 63 rpm. The apparatus measures the time it takes for the polymer to degrade, as shown by an increase of torque due to crosslinking of the polymer chains.

RESULTS AND DISCUSSION

The results of the static test are reported in Figure 1, and they show that zinc maleate and, particularly, zinc anthranilate are good thermal stabilizers for PVC. The graph has a maximum at 2% concentration of the zinc compound in the stabilizer.

When the acive chlorine atoms in the polymer are substituted by anthranilate and maleate groups, zinc chloride is produced, and since it is a Lewis acid, it removes HCl from the polymer chains accelerating their degradation. This is why costabilizers are required (phosphites and epoxidized oil), which inactivate $ZnCl_2$ by coordination.[9]

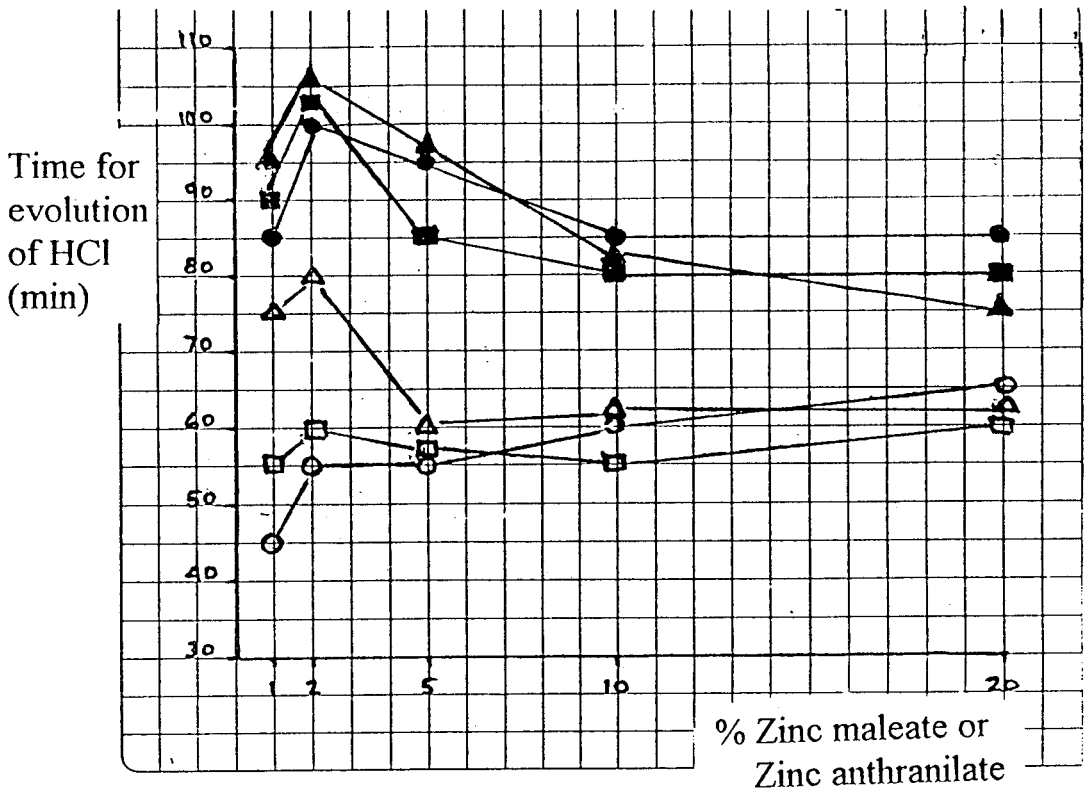

Figure 1 Results of the Congo Red test. Time for the evolution of HCl versus percentage of the zinc compound in the mixture with calcium stearate. The solid circles, squares, and triangles correspond to zinc anthranilate, and the open ones, to zinc maleate. See Table I for the formulations represented by the symbols.

The other costabilizer, calcium stearate, reacts with $ZnCl_2$ and produces calcium chloride and zinc stearate, which is capable of substituting active chlorine atoms and thus continue the stabilizing action[9,10]:

$$Ca(OOCR)_2 + ZnCl_2 \rightarrow CaCl_2 + Zn(OOCR)_2$$

Calcium chloride is not a Lewis acid and it does not cause any damage to the polymer.

The concentration of the zinc compound in the stabilizer must be sufficient for the substitution of active chlorine atoms at a proper speed, but must not overcome the capacity of calcium stearate to convert zinc chloride into zinc stearate. This explains the maxima in the graphs of Figure 1.

The results of the static test do not guarantee that a compound will be a good stabilizer in actual processing, because in those tests, no shear forces are involved. That is why the dynamic test was performed under the following conditions:

Temperature	180ºC
Rotors	Roller type
Speed	63 rpm.
Formulation	100 PVC
	2 Phosphite
	3 Epoxidized oil
	4 Ca/Zn stabilizer containing
	2% zinc compound.

The results were

Zinc Compound	Dynamic Stabilization Time (min)
Maleate	13.7
Anthranilate	17.8

CONCLUSIONS

1. Zinc maleate and zinc anthranilate are good stabilizers for PVC in combination with calcium stearate, diphenyl isodecyl phosphite, and epoxidized soya oil, as demonstrated by the results of the static and dynamic tests.
2. Zinc anthranilate is more effective than is zinc maleate.
3. It is important to use no more than 2% of the zinc compound in the mixture with calcium stearate, as the stabilizing performance drops with higher concentrations of the zinc compound.

REFERENCES

1. Encyclopedia of PVC; Nass, L. I., Ed.; Marcel Dekker: New York, 1977; Vol. I, Chapter 9.
2. W. S. Penn, PVC Technology; Applied Science: London, 1971.
3. Close, L. G.; Gilbert, R. D. Polym Plast Technol Eng 1977, 8, 177.
4. Caraculaco, A. A. Pure Appl Chem 1981, 53, 385.
5. Naqvi, M. K. JMS Rev Macromol Chem Phys C 1985, 25, 119.
6. Ureta, E. Estabilizadores Térmicos y Otros Aditivos Para PVC; Editorial Limusa-Noriega: México City, 1989.
7. Rasuvaev, G. A.; Troitskaya, L. S.; Troitskii, B. B. J Polym Sci A-1 1971, 9, 2673.
8. Culp, E. Mod Plast Int 1994, Sept., 72–75.
9. Onozuka, M. J Polym Sci A-1 1967, 5, 2229.
10. Anderson, D. F.; Mckenzie, D.A. J Polym Sci 1970, A-1, 8, 2905.