Effect of Metal Cyanourates on Some Properties of PVC

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Synopsis

The effects of barium, lead and calcium cyanourate on the properties of poly(vinyl chloride) and its compositions were investigated. In concentrations up to 2 vol. % they decreased the T_g and T_m of the polymer. Physical and mechanical properties (tensile strength, impact strength, and hardness) are improved. The thermostability (dynamic and static) increases with increasing concentration.

INTRODUCTION

The improvement in properties and processability of PVC compounds, as well as thermostability in the time–temperature range, is related to the use of new effective stabilizers. Generally heavy metal salts are used as stabilizers.

The purpose of the present investigations was to study the influence of new synthesized[5] metal salts (Ph,Ba,Ca) of cyanuric acid on the complex properties of PVC and its compositions and to determine their stabilizing effect.

INVESTIGATION OBJECTS AND METHODS

PVC suspension type-68 and properties according to BDS 8807-71 were used in our investigation.

The properties of the metal cyanourates used are listed in Table I. Thermomechanical tests were carried out on a dynamometric balance.[6]

TABLE I
Characteristics of the Metal Cyanourates

Product type	Empirical formula	Density (kg/m^3)	Losses up to 500° (%)	Free acid and alkaly (%)	Melting temp (°C)	Content of basic comp. (%)
1. Calcium cyanourate	$Ca_3(C_3N_3O_3)_2$	1.430	4	None	Above 350	95
2. Barium cyanourate	$Ba_3(C_3N_3O_3)_2$	3.210	6	None	Above 350	95
3. Lead cyanourate	$Pb_3(C_3N_3O_3)_2$	6.210	15	None	Above 350	95

Note: The losses are determined on derivatograph, Paulic-Erdi.

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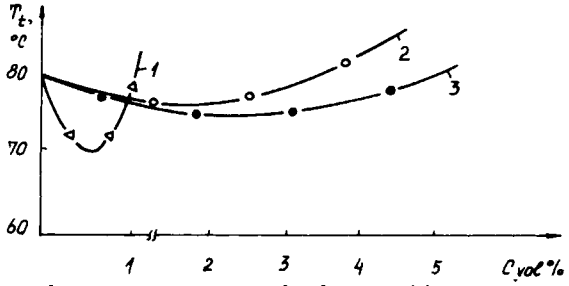

Fig. 1. Effect of metal cyanourate content on the glass transition temperature of PVC: (1) lead cyanourate; (2) barium cyanourate; (3) calcium cyanourate.

Physical tests were accomplished on the "Instron" TT-M machine at deformation rates of 50 mm/min.

Tests for dynamic thermostability and equilibrium moment of rotation were carried out on the "Brabender" plastograph type PLV-131 under the following conditions: temperature = 185°C; shaft revolutions = 60 rev/min; feed material quantity in the kneader = 37 g. Static thermostability was determined according to BDS.

RESULTS AND DISCUSSION

The temperatures of the physical transitions in PVC are of great importance for the intended application and polymer composition processing. The glass transition temperature could be related to the distribution of the additives in the polymer and their effect on the relaxation transitions.

The thermomechanical test results show that the metal cyanourates (lead, barium, calcium) decrease the PVC glass transition temperature (T_g) (Fig. 1) by about 5–10°C at 0.5 vol % lead cyanourate and 2 vol % barium and calcium cyanourates. Above these concentrations there is no significant change.

The melting temperature (T_m) (Fig. 2) is also decreased by about 10–15°C, but the range of high elasticity is not changed considerably.

The observed variations in T_g and T_m can be explained by analogy with the distribution of the other metal salts, used as stabilizers.

The T_g decrease at low contents of metal salts shows a decrease in the PVC intermolecular interactions, which is a precondition for an increase of the structural elements and supermolecular formation mobility in the polymer.

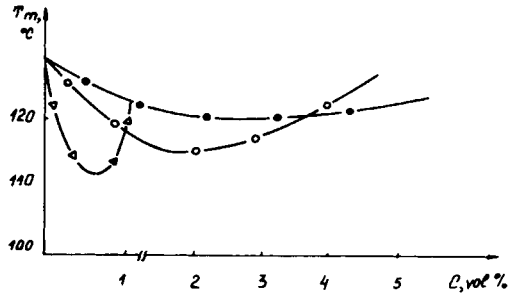

Fig. 2. Effect of metal cyanourate content on the melting temperature of PVC: (△) lead cyanourate; (○) barium cyanourate; (●) calcium cyanourate.

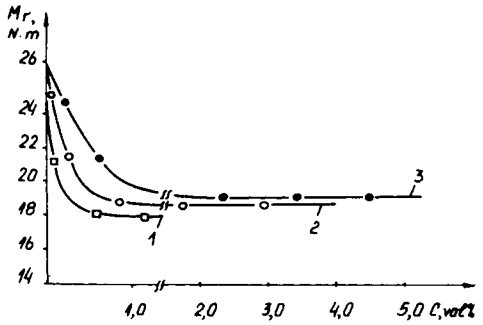

Fig. 3. Effect of metal cyanourate content on the equilibrium moment of rotation of PVC: (1) lead cyanourate; (2) barium cyanourate; (3) calcium cyanourate.

According to the current concepts[7] about the structural model, in the polymer (PVC) there are a different arranged supermolecular structural formations, connected by transient chains with length and thickness less than in the arranged ones. The additives in low concentrations (lead, barium, and calcium cyanourates) are distributed in these intermolecular loose regions. In this way, they have an effect on the flexibility and conformation transitions of the transient chains and supermolecular structure.

The increase in the T_g when the cyanourate content increase shows quite the contrary, a decrease in both the macromolecular mobility and supermolecular formation. Also, it is possible for donor–acceptor interactions to arise with the dispersion additive surface, which effects the relaxation processes.

Data determined by the "Brabender" plastograph show that the equilibrium moment of rotation (Fig. 3) sharply decreases up to contents of 1 vol % for all three salts. In this respect, the lead cyanourate has the strongest effect. Data correlates with T_g and T_m.

The polymer thermostability {dynamic [Fig. 4(a)] and static, [Fig. 4(b)]} showed differences between dynamic and static thermostability, when determined by the two methods.

Dynamic thermostability increases up to 1 vol % content and then levels off. In relation to their activity the metal cyanourates are arranged in the following sequence: Ca-cyanourate, Ba-cyanourate, Pb-cyanourate. Above 1–2 vol % content of Ca-cyanourate, the thermostability decreases, and with Ba-cyanourate increases sharply. Static thermostability is in the reverse order (Pb-cyanourate, Ba-cyanourate, Ca-cyanourate). That can be exlained by the thermodynamic influence in the first case, the thermal, in the second. Because of the weaker dipole–dipole interaction between the Ca-cyanourate and the polar PVC, there is lubrication action and decrease in friction heat. An opposite effect was observed with lead cyanourate, which has acceptor properties of Pb^{++}. However, at static thermostability, the destruction process becomes difficult due to the limited heat movement of the C—Cl links, which causes polarization, and dehydrochlorination occurs at higher temperatures and longer heating time. This results in an increase in activation energy in PVC during dehydrochlorination and thermostability.

The investigation data with respect to one effect of metal cyanourates on PVC mechanical properties [Fig. 5(a) and (b)] shows that the tensile strength (Fig. 5) is increased with all three salts up to contents of 0.4 vol % lead cyanourate and

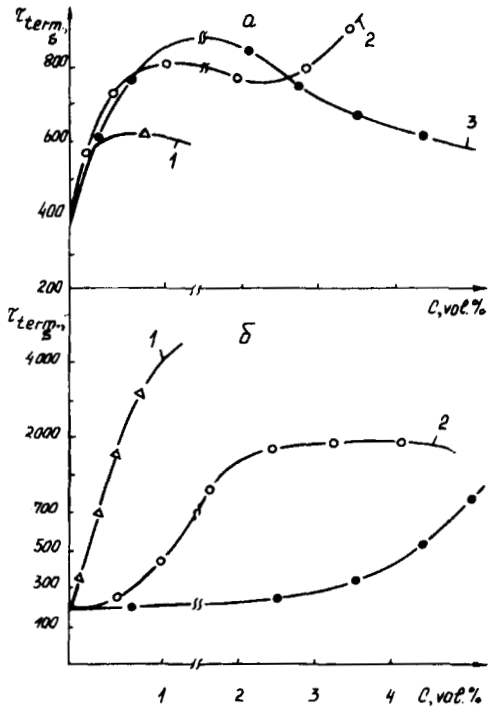

Fig. 4. Effect of metal cyanourate content on the dynamic (a) and static (b) thermostability of PVC: (1) lead cyanourate; (2) barium cyanourate; (3) calcium cyanourate.

2.5 vol % barium cyanourate and calcium cyanourate. Above these concentrations a decrease in the tensile strength is observed.

Specific elongation [Fig. 5(b)] increases at low concentrations (up to 0.2% vol

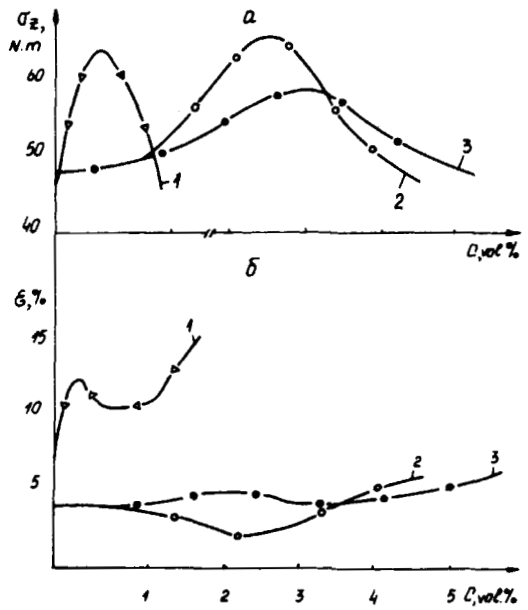

Fig. 5. Effect of metal cyanourate content on the tensile strength (a) and specific elongation (b) of PVC: (1) lead cyanourate; (2) barium cyanourate; (3) calcium cyanourate.

TABLE II
Effect of Metal Cyanourates on the Properties of PVC Compositions

Property	Measure	PVC composition for Pipe				PVC composition for Insulation			
		Without metal cyanourates	With metal cyanourates			Without metal cyanourates	With metal cyanourates		
			Ba	Ca	Pb		Ba	Ca	Pb
			0.5 wt %	0.5 wt %	0.5 wt %		2 wt %	2 wt %	2 wt %
1. Tensile strength	MPa	43	71.6	68	58.8	18	32	28	25.8
2. Specific elongation	%	12	16.4	18.1	18	179	220	215	208
3. Modulus of elasticity	MPa	850	980	860	900	—	—	—	—
4. Impact strength		2.1	3.0	3.4	3.2	—	—	—	—
5. Brinel hardness	MPa	61	113	108	89	—	—	—	—
6. Vicat softening point	°C	94	99	96	98	—	—	—	—
7. Cold resistance	°C	—	—	—	—	−30	−35	−37	−34
8. Specific volume resistance—20°	ohm/m	—	—	—	—	1×10^{14}	391×10^{15}	1×10^{15}	8.3×10^{14}
9. Specific volume resistance—70°	ohm/m	—	—	—	—	1×10^{12}	9×10^{12}	6×10^{12}	4.3×10^{12}
10. Electrical resistance	kV/m	—	—	—	—	15	26	25	24
11. Thermal deformation	%	—	—	—	—	30	27	26	25
Properties after aging									
12. Tensile strength	MPa	58.8	76	70	66.2	80	93	96	95
13. Specific elongation	%	14	14	16.2	13.4	83	95	97	96

%) of lead cyanourate only, but with the other two salts significant variations are not observed; the deformation is kept nearly constant.

As high dispersive and high melting additives, the metal cyanourates effect on the polymer mechanical properties are like active fillers. Because of their polar character they contribute to an increase in macrochains and structural formations. They also densify the structure and give rise to the additional physical units between macrochains, which leads to an increase in strength properties.

The investigation results recommended these cyanourates for use as thermostabilizers and structural modifiers for PVC compositions.

In order to check the results, the metal cyanourates were introduced in flexible and rigid PVC compositions as a third component of the stabilizing system.

With all three metal cyanourates (barium, calcium, lead) (Table II) the mechanical properties are improved and the dynamic thermostability is increased. This is due to the fact that the cyanourates behave as thermostabilizers and structural modifiers.

The results of the investigation of the two-component and multicomponent compositions show that metal cyanourates can be used as stabilizing additives in conjunction with other stabilizers in PVC compositions.

CONCLUSIONS

The effect of the Pb-, Ba-, and Ca-cyanourates on the properties of PVC was investigated. It was found that

(1) The addition of 0.5 to 2 vol % metal cyanourates decreases T_g and T_m and equilibrium moment of rotation in PVC.

(2) The addition of Pb-, Ba-, and Ca-cyanourates leads to an improvement in the mechanical properties and dynamic thermostability of PVC.

(3) The results recommend the use of Pb-, Ba-, and Ca-cyanourates as thermostabilizers and structural modifiers in PVC compositions.

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