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Preparation of Metal Carboxylates and Their Stabilizing Performance under Intense High-Pressure Shear Treatment

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Abstract—Solid-phase synthesis of certain metal carboxylates and their effect on stabilization of polyvinyl chloride under intense high-pressure shear treatment were studied.

Metal carboxylates are widely used as thermal stabilizers and lubricants in development of new materials and goods based on polyvinyl chloride (PVC) [1]. The main method of industrial production of metal carboxylates is the exchange reaction between aqueous solution of metal chloride or nitrate and sodium carboxylate, e.g., stearate, at elevated temperatures. It is characterized by a large amount of wastewater, the need in additional operations to isolate target products, etc. [2]. In known methods of solid-phase synthesis of metal carboxylates [3, 4], sophisticated and power-consuming devices with abrasive, cutting, and impact action are used. The product yields in such procedures are usually low.

A new method of solid-phase synthesis of chemical materials and processing and modification of polymers under intense high-pressure shear treatment (IHPST) at elevated temperatures in special dispersers is being actively developed today [5, 6]. Under IHPST, various chemical reactions can proceed in polymers: change of supramolecular structure, disintegration, and increase in specific surface area of the material treated with formation of a superfine powder.

The goal of this work is to perform solid-phase synthesis of certain metal carboxylates and to study polyvinyl chloride (PVC) stabilization with these carboxylates under IHPST.

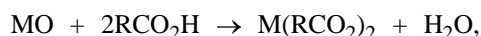
EXPERIMENTAL

The solid-phase synthesis of metal carboxylates and processing of polyvinyl chloride compositions under IHPST were performed in a rotary disperser designed at the Institute of Chemical Physics, Russian

Academy of Sciences [6]. The yield of metal carboxylates was determined analytically in accordance with TU (Technical Specifications) 6-09-4104–87 from the residual content of carboxylic acids in the reaction mixture and by IR spectrometry on a Bruker IFS-88 spectrometer from the intensity of the absorption bands within the 1400–1650 cm⁻¹ range depending on metal. Pure grade stearic, lauric, and palmitic acids and calcium, barium, cadmium(II), lead(II), and zinc(II) oxides or their binary mixtures, and sodium and potassium carbonates were used. The method of determination of the PVC dehydrochlorination rate was similar to that described in [7]. The thermal stability time of polymeric compositions was determined in accordance with GOST (State Standard) 14 041–91.

The IHPST method has no disadvantages characteristic for other methods of metal carboxylate synthesis and provides high yield of the reaction products and short reaction time; no catalysts are required. The specific feature of solid-phase reactions with IHPST is that the combined effect of high pressure and shear strain brings solid substances to the plastic flow state. In the process, a great amount of structural defects is formed in the substance, electronic properties of molecules change, and the activation barrier of reactions decreases [8].

The solid-phase synthesis of metal carboxylates proceeds by the reactions



where M = Ca, Ba, Zn, Cd, Pb; M' = K, Na; R = C₁₁H₂₃, C₁₅H₃₁, C₁₇H₃₅.

The reaction products are formed during passing of the reaction mixture through the rotary disperser for 3–5 min at a single IHPST effect on the reactants. The yield of the target product, which is obtained as a dry superfine powder, was 96–99% of the calculated amount (Table 1). The method allows preparation in the same device of a wide assortment of individual metal carboxylates and their mixtures (including synergistic mixtures).

Estimation of the stabilizing performance of salts of saturated monocarboxylic acids with respect to vinyl chloride polymers (PVC; copolymer of vinyl chloride with 4 wt % propylene, VCPR-4; copolymer of vinyl chloride with 15 wt % vinyl acetate, VCVA-15) showed that, with respect to the “thermal stability time” index, it is not inferior to the performance of stabilizers prepared by the industrial method (Table 2).

The solid-phase method of obtaining metal carboxylates under IHPST has substantial advantages as compared to the industrial synthesis method: it is continuous and single-stage, synthesis can proceed in one apparatus at a high rate without heating, the process is characterized by elevated environmental safety, and the chemical modification of stabilizers and preparation of synergistic mixtures on their base are possible.

The synthesis of metal carboxylates is also possible directly in a polymer matrix, when a mixture of PVC with a metal oxide (or another base) and an equivalent amount of a carboxylic acid is processed in a rotary disperser. The high stabilizing performance of the components under IHPST is apparently due to solid-phase synthesis of metal carboxylates from the initial reactants. It should be noted, however, that, with the carboxylates prepared *in situ*, the thermal stability time is shorter than when PVC is stabilized with the corresponding metal carboxylates prepared in advance (Table 3).

To improve PVC grinding under IHPST, various components, in particular, metal carboxylates can be used as process additives. Joint grinding of PVC mixtures with metal carboxylates under IHPST substantially improves the process efficiency and increases the degree of dispersion of the powder formed.

Joint grinding of PVC with metal carboxylates under IHPST substantially enhances stabilizing performance of additives with respect to thermal stability time index as compared to usual mechanical mixing (Table 3). The stabilizing performance of additives also increases with respect to the “dehydrochlorination rate” index when coordination-unsaturated metal

Table 1. Solid-phase synthesis of metal carboxylates under IHPST

Reactants used		Molar ratio acid : metal oxide (salt)	Product yield, %
acid	metal oxide, salt		
C ₁₇ H ₃₅ CO ₂ H	CaO	2 : 1	99
	CaO	2 : 1	98
	CaO	2 : 1	98
	CaO	2 : 1	99
	BaO	2 : 1	96
	ZnO	2 : 1	97
	PbO	2 : 1	96
	CdO	2 : 1	98
C ₁₁ H ₂₃ CO ₂ H	CaO	2 : 1	98
	CdO	2 : 1	97
C ₁₅ H ₃₁ CO ₂ H	BaO	2 : 1	97
	PbO	2 : 1	96
C ₁₇ H ₃₅ CO ₂ H	K ₂ CO ₃	2 : 1	96
	Na ₂ CO ₃	2 : 1	97
	BaO + CaO	4 : 1 : 1	96
	CaO + ZnO	4 : 1 : 1	97

Table 2. Effect of metal carboxylates synthesized under IHPST conditions (2 wt parts per 100 wt parts of polymer) on the thermal stability time of vinyl chloride polymers

Metal carboxylate	Thermal stability time, min		
	PVC	VCPR-4	VCVA-15
–	4	4	3
Stearate of:			
calcium	21(22)*	20(19)	17(18)
barium	57(56)	55(54)	51(52)
zinc	5(5)	4(4)	3(4)
lead	76(75)	72(73)	68(70)
cadmium	31(32)	29(29)	26(27)
Laurate of:			
calcium	25(26)	23(22)	20(19)
cadmium	36(35)	33(34)	29(27)
Palmitate of:			
barium	61(61)	59(58)	55(54)
lead	79(79)	74(72)	70(69)
Stearate of:			
potassium	58(57)	55(56)	52(50)
sodium	62(63)	58(60)	55(56)
Mixture of stearates:			
barium and calcium	46(44)	44(45)	41(42)
calcium and zinc	19(20)	18(18)	15(15)

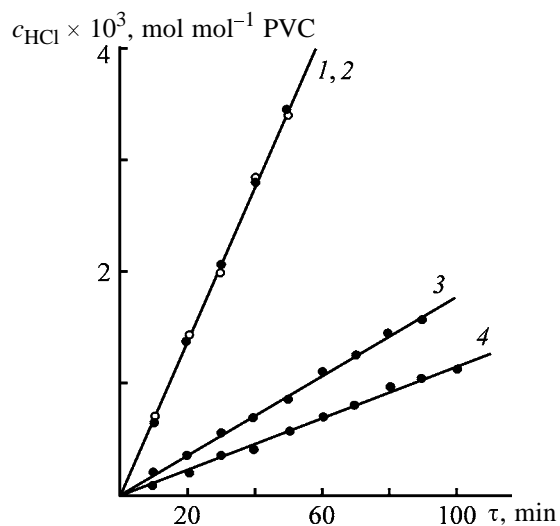
* The thermal stability time of vinyl chloride polymers (175°C) in the presence of metal carboxylates synthesized by the industrial method is given in parentheses.

Table 3. Change in thermal stability time and rate of PVC dehydrochlorination in the presence of additives after IHPST*

Component	Composition, wt %, for indicated sample												
	1	2	3	4	5	6	7	8	9	10	11	12	13
PVC	100	100	100	100	100	100	100	100	100	100	100	100	100
(C ₁₇ H ₁₉ CO ₂) ₂ Ba	5	–	–	–	–	–	–	–	–	–	–	–	–
(C ₁₇ H ₁₉ CO ₂) ₂ Ca	–	3	5	–	–	–	–	–	–	–	–	–	–
C ₁₇ H ₁₉ CO ₂ Na	–	–	–	5	–	–	–	–	–	–	–	–	–
(C ₁₇ H ₁₉ CO ₂) ₂ Pb	–	–	–	–	3	5	–	–	–	–	–	–	–
(C ₁₇ H ₁₉ CO ₂) ₂ Cd**	–	–	–	–	–	–	5	–	–	–	–	–	–
(C ₁₅ H ₁₇ CO ₂) ₂ Ba	–	–	–	–	–	–	–	3	–	–	–	–	–
BaO	–	–	–	–	–	–	–	–	1.08	–	–	–	–
CaO	–	–	–	–	–	–	–	–	–	0.46	–	–	–
NaOH	–	–	–	–	–	–	–	–	–	–	0.64	–	–
PbO	–	–	–	–	–	–	–	–	–	–	–	1.44	–
CdO**	–	–	–	–	–	–	–	–	–	–	–	–	0.94
C ₁₇ H ₁₉ CO ₂ H	–	–	–	–	–	–	–	–	4.04	4.70	4.64	3.67	4.20
Thermal stability time at 175°C, min:													
before IHPST	97	24	50	153	64	274	105	74	48	18	115	75	50
after IHPST	109	32	58	171	73	282	118	85	84	43	143	181	88
V _{HCl} × 10 ⁶ at 175°C, mol HCl : mol PVC*:													
before IHPST	1.20	1.20	1.20	1.21	0.32	0.30	0.32	1.19	1.33	1.46	1.70	0.85	1.06
after IHPST	1.21	1.19	1.20	1.22	0.21	0.18	0.24	1.18	1.26	1.28	1.31	0.39	0.52

* Temperature in disperser at IHPST: in compression chamber 115°C and in grinding chamber 60°C; speed of screw rotation 35 min⁻¹.

** Dehydrochlorination rates in the initial period of degradation.



Kinetics of dehydrochlorination (175°C, air) of PVC stabilized (5 wt parts per 100 wt parts of PVC) with (1, 2) barium stearate and (3, 4) lead stearate (1, 3) before and (2, 4) after intense high-pressure shear treatment in a rotary disperser; (c_{HCl}) hydrogen chloride concentration and (τ) time.

[Cd(II) and Pb(II)] stearates are used, which, in addition to HCl scavenging, inhibit PVC dehydrochlorination due to chemical deactivation of the labile groups [7] (Table 3).

The physical and chemical processes occurring under IHPST are characterized by high rate of mass transfer (apparent diffusion coefficient becomes several times higher [8]). In this case, increased stabilizing performance of metal carboxylates can be explained by more uniform distribution of the thermal stabilizer in the polymer and by better accessibility of labile groups in reaction with stabilizing additives.

CONCLUSION

The method of intense high-pressure shear treatment shows promise in solid-phase synthesis of metal carboxylates. It also enhances their stabilizing performance in processing of polymeric compositions based on polyvinyl chloride.

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