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INTERNAL CORRESPONDENCE

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Date: October [illegible], 19[illegible]
Originating Dept. Applications - [illegible]
Answering letter date
Subject: Polymerization Processes

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Attached for your reference is an article entitled "Mass Polymerization of Vinyl Chloride in the Presence of Acceptors of Hydrogen Chloride" from Soviet Plastics of June 19[illegible]. They conclude that the introduction of HCl acceptors into the reaction medium will accelerate polymerization. Also the addition of stabilizing additives in the reaction will increase the stability and reduce degree of branching.

This may be of value in our non-solvent process or contemplated Pechiney-St. Gobain Process. Could our intermittent problems on the thermal stability of suspension resins be related to HCl in the monomer?

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nate indicate that the addition of 0·1% benzoyl peroxide gives a slight increase in the time of gel formation.

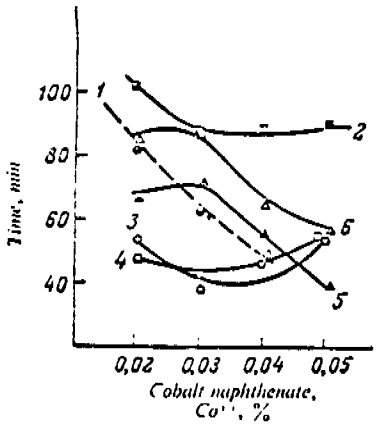

Fig. 6—Dependence of the gel formation time on the composition of the initiating systems: 1—0·2% methylethylketone peroxide; 2—0·2% methylethylketone peroxide + 0·1% benzoyl peroxide; 3—0·2% methylethylketone peroxide + 0·2% benzoyl peroxide; 4—0·2% methylethylketone peroxide + 0·5% benzoyl peroxide; 5—0·2% methylethylketone peroxide + 0·8% benzoyl peroxide; 6—0·2% methylethylketone peroxide + 1·0% benzoyl peroxide.

On increasing the amount of benzoyl peroxide to 0·2–0·5% we observe a reduction in the gel formation time, but a further increase to 0·8–1% gives an increase in this time (Fig. 6). The degree of hardening in this case either remains at the same level or increases somewhat; the mechanical properties basically remain without change. This discrepancy with the data in the literature may be a result of the use of peroxides of different grades or of different methods of hardening.

It is well known that the gel formation time may be considerably reduced by adding a tertiary amine to an initiator system consisting of a peroxide or hydroperoxide initiator and a cobalt hardener.

We investigated the influence of the co-accelerator diethylaniline on the gel formation time and the degree of hardening of PNA-ED-2 polyester resin when using the following initiating systems: isopropylbenzene hydroperoxide—cobalt naphthenate; methylethylketone peroxide—cobalt naphthenate. It was found that the addition even of small amounts of diethylaniline (0·02%) leads to a marked reduction in the gel formation time (to 10 min). A further increase in the amount of co-accelerator has little effect on the rate of gel formation of PNA-ED-2 resin. The mechanical properties remain on the same level as when using systems with one accelerator, while the degree of hardening is reduced in many cases.

Since acceleration of gel formation is possible when using systems with one accelerator, the addition of a co-accelerator is desirable only where the hardening of the resins has to be carried out at temperature below 20°C.

Conclusions

1. For the cold hardening of PNA-ED-2 resin the most suitable are two-component systems based on methylethylketone and cyclohexanone peroxides with a cobalt accelerator.

2. Three-component systems (methylethylketone peroxide—benzoyl peroxide—cobalt naphthenate and cyclohexanone peroxide—isopropylbenzene hydroperoxide—cobalt naphthenate) have no advantages over two-component systems.

3. The use of diethylaniline as a supplementary accelerator in the systems isopropylbenzene hydroperoxide—cobalt naphthenate and methylethylketone peroxide—cobalt naphthenate gives a marked reduction in the gel formation time without changing the mechanical properties.

Bibliography

1. Z. V. Mikhaĭlova and P. Z. Li, Soviet Plast. No. 1, 1964 (translation of Plast. Massy, No. 1, 1963), p. 13.
2. I. W. Cywinski, Appl. Plast., 3, 2, 1960, p. 56 (sic).
3. I. W. Cywinski, Reinf. Plast., 4, 8, 1960, p. 8.
4. P. Z. Li *et al.*, Plast Massy, No. 2, 1959, p. 19.
5. I. W. Cywinski and P. Stopp. Kunstst. Rundschau, 8, 12, 1961, p. 593.
6. S. I. Omel'chenko *et al.*, Soviet Plast., No. 2, 1965 (translation of Plast. Massy, No. 2, 1964), p. 20.

Mass polymerisation of vinyl chloride in the presence of acceptors of hydrogen chloride

V. I. Tomashchuk, I. B. Kotlyar, A. M. Sharetskiĭ and E. N. Zil'berman

Translated by R. J. A. Hendry

THE production of PVC by polymerisation of vinyl chloride in the mass is of interest because of the brevity of the process. There is no need for an aqueous dispersion medium, emulsifiers or emulsion stabilisers, and the stages of filtration of the suspension and drying of the polymer, occurring in the usual emulsion and suspension methods will also be obviated.

The major obstacle preventing the widespread industrial use of this method arises out of difficulties in uniform removal of the polymerisation heat with consequent local overheating, and dehydrochlorination of the polymer. Therefore the PVC produced by polymerisation of vinyl chloride in the mass usually has low heat-resistance, a wide molecular weight distribution and probably a more branched structure. When the degree of conversion exceeds 60–65% the quality of the polymer is reduced still further[1], and the heat removal is greatly impaired because of the virtual absence of a liquid phase.

To improve the quality of the polymer, additives which combine with hydrogen chloride[2] are added to the monomer.

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The present authors studied the effect of certain compounds used generally as stabilisers of PVC (stearates of lead, barium, cadmium, calcium and also epoxy compounds) on the polymerisation of vinyl chloride in the mass, and investigated certain properties of the polymer.

Experimental method

The vinyl chloride was polymerised in a horizontal rotating cylindrical 10 l. reactor of Kh 18 N steel. Mixing was effected by means of a roller which rolled around the cylinder wall as the reactor rotated.

To 100 parts (by weight) of the monomer 0·2 parts of α,α′-azobisisobutyronitrile were taken (or 0·25 parts of lauryl peroxide), and also $6·5 \times 10^{-4}$ mol of the metal stearates (or 0·625 g of an epoxy compound). The reagents were added to the reactor immediately before the vinyl chloride.

The amount of the additives was determined as follows. An empirical method was used (with lead stearate as an example) to determine the least amount of the stabiliser ($6·5 \times 10^{-5}$ mol ph parts of the monomer) which would ensure the highest yield of the polymer in a certain time. However, on investigation of the properties of the PVC it was difficult to determine the very small amount of metal stearate remaining in the polymer after several reprecipitations from a 1% solution in cyclohexanone. It was therefore necessary to increase the content of metal stearates to $6·5 \times 10^{-4}$ mol.

The Huggins constant (k^1) was calculated[3] from the data obtained. The PVC was reprecipitated from 1% solution in cyclohexanone with cooled methanol.

The kinetics of the decomposition of α,α′-azobisisobutyronitrile in the presence of lead stearate were determined in toluene by the amount of nitrogen evolved[5,6]. The rate of polymerisation of vinyl chloride in the presence of HCl was determined in ampoules, the polymer formed being weighed a certain time after the ampoules had been opened.

Discussion of results

The kinetics of the polymerisation of vinyl chloride in the mass in the presence of HCl acceptors are shown in Fig. 1.

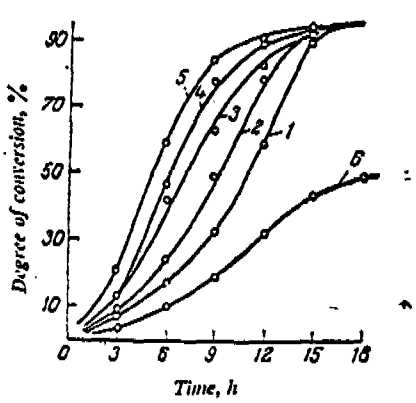

Fig. 1—Kinetics of polymerisation of vinyl chloride in the mass at 50°C in the presence of acceptors of HCl (initiator: α,α′azobisisobutyronitrile). HCl acceptor: 1—none; 2—calcium stearate; 3—aliphatic epoxy compound; 4—barium stearate or cadmium stearate; 5—lead stearate; 6—ED-5 epoxy resin.

It will be seen that the rate of polymerisation of vinyl chloride increases in the presence of certain additives, but not to the same extent in each case.

Certain epoxy compounds[4,7,8] are effective stabilisers of PVC. Fig. 1 shows that ED-5 resin has an inhibiting effect on the polymerisation of vinyl chloride, which is probably due to the presence of phenolic residues in the ED-5. On the other hand the addition of an aliphatic epoxy compound (a product of the condensation of epichlorohydrin and ethylene glycol) noticeably increases the rate of polymerisation of vinyl chloride.

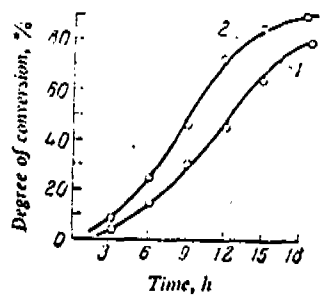

Fig. 2—Kinetics of polymerisation of vinyl chloride in the mass at 50°C (initiator: lauryl peroxide): 1—without HCl acceptor; 2—in presence of lead stearate.

Fig. 2 shows the kinetics of the polymerisation of vinyl chloride in the mass with lauryl peroxide as initiator. In this case also the rate of polymerisation of vinyl chloride is appreciably increased in the presence of lead stearate.

The increase in the rate of polymerisation of vinyl chloride may be due to the combination of the HCl, which is probably capable of inhibiting polymerisation.

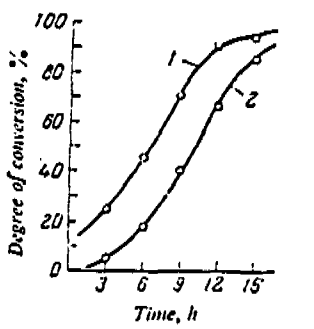

Fig. 3—Kinetics of polymerisation of vinyl chloride in the mass at 50°C (initiator: α,α′-azobisisobutyronitrile): 1—in absence of HCl; 2—in presence of HCl (0·8% on weight of monomer).

To verify this a study was made of the rate of polymerisation of vinyl chloride in the presence of HCl. Fig. 3 shows that the rate is noticeably reduced by the presence of 0·8% of HCl on the weight of the monomer. Moreover in view of the increased rate of polymerisation of vinyl chloride in the presence of stabilising additives, there is a suggestion of their accelerating effect in the decomposition of the α,α′-azobisisobutyronitrile. The rate constant of decomposition of α,α′-azobisisobutyronitrile in the presence of lead stearate was therefore determined (Table 1).

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Table 1 shows that the constant of the rate of decomposition does not increase in the presence of lead stearate.

TABLE 1
Rate of breakdown of α, α'-azobisisobutyronitrile in presence of lead stearate in toluene

Amount of lead stearate, mol per mol of initiator	*Temperature, °C*	$k \times 10^4$, sec^{-1}
0	84	3·0
$7{\cdot}74 \times 10^{-4}$	84·10	3·6
$7{\cdot}74 \times 10^{-4}$	83·8	2·8
$7{\cdot}74 \times 10^{-3}$	84	3·1

The values of k given in the Table agree well with the published data[6] obtained in a study of the decomposition of α,α'-azobisisobutyronitrile without additives; consequently, the lead stearate present in the polymerisation medium has no effect on the rate of decomposition of the initiator.

The combination of the hydrogen chloride evolved during polymerisation of vinyl chloride may affect not only the rate of the reaction but also the properties of the polymer.

It was shown in [4] that even a low degree of dehydrochlorination of the polymer further increases its sensitivity to various factors, particularly that of temperature. Therefore the suppression of dehydrochlorination in the polymerisation of vinyl chloride should improve the heat stability of the polymer, which is confirmed by Table 2.

TABLE 2
Heat stability and decompostion temperature of PVC produced in presence of lead stearate (0·59% on weight of polymer)

No. of reprecipitation	*Characteristics*	*PVC produced in presence of a stabiliser*	*PVC mixed with a stabiliser*	*PVC without a stabiliser*
0	Decomposition temperature, °C	170	171·5	125
	Heat stability, min	10	12	1·5
	Lead content, %	0·155	0·16	—
		167	165	144
1	Ditto	20	3·8	1·5
		0·07	0·12	—
		173	167·5	142
2	Ditto	17·5	4·0	1·6
		0·04	0·033	—
		166·5	164	140
3	Ditto	10·5	1·75	1·5
		Nil	Nil	—
		166	—	—
4	Ditto	10	—	—
		Nil	—	—
		166	—	—
5	Ditto	10	—	—
		—	—	—

The PVC produced in the presence of lead stearate and with subsequent complete removal of the latter by means of repeated reprecipitation from cyclohexanone retains its high decomposition temperature and heat stability. At the same time PVC produced in the absence of lead stearate but mixed with it in the mixer, after reprecipitation under the same conditions loses the high heat stability of the mixture.

Thus Table 2 shows that PVC produced in the presence of an HCl acceptor acquires higher intrinsic heat stability. The higher decomposition temperature of the PVC mixed with the stabiliser and then reprecipitated, compared with the decomposition temperature of the initial PVC, is probably due to partial washing out of low-molecular fractions of the polymer during reprecipitation.

TABLE 3
Intrinsic viscosity and Huggins' constants of PVC produced without additives, and with lead stearate added to polymerisation medium

No. of experiment	*Content of lead stearate in PVC, %*	*Degree of conversion of monomer, %*	*Intrinsic viscosity, [η]*	*Huggins' constant, k*
1	0	60	0·855	0·62
2	0	60	0·86	0·61
3	0	70	0·83	0·55
4	1·48	60	1·12	0·32
5	0·785	85	1·06	0·36
6	1·00	83	0·94	0·40

Table 3 gives the data on the intrinsic viscosity of PVC produced without additives, and also with the addition of lead stearate; also the calculated Huggins' constants, indicating the relative branching of the polymer[3]. It shows that PVC produced without HCl acceptors has macromolecular structure with a considerably higher degree of branching. At the same time relatively greater linearity of the structure is obtained even with a conversion adjusted to 83–85% (experiments 5,6) when considerable overheating should occur in places on account of poor heat transfer.

Conclusions

1. In view of the inhibiting action of HCl on the polymerisation of vinyl chloride, the introduction of HCl acceptors into the reaction medium accelerates the polymerisation.

2. The introduction of stabilising additives in the polymerisation of vinyl chloride in the mass increases the intrinsic stability of the polymer, and reduces the degree of branching.

Bibliography

1. I. B. Kotlyar and A. M. Sharetskii, Soviet Plast., No. 2, 1966, (translation of Plast. Massy, No. 2, 1965).
2. K. Bik, Polimery, No. 7–3, 1962, p. 244.
3. M. Imoto, J. Soc. Organic Chem. (Japan), 14, No. 1, 1956, p. 10–19.
4. G. Ya. Gordon, "Stabilisation of synthetic high polymers", 1963, translation in English, 1964.
5. C. G. Overberger *et al.*, J. Am. Chem. Soc., 71, 1949, p. 2661.
6. C. H. Bamford, W. G. Barb, A. D. Jenkins and P. F. Onyon, "Kinetics of vinyl polymerisation by radical mechanisms", 1958, (Russian version, 1963), p. 248.
7. E. N. Zil'berman, "Progress in polymer chemistry and technology", No. 3, 1960, p. 83.
8. "Ageing and stabilisation of polymers", ed. M. B. Neiman, 1964, p. 133.

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