

Polymerization of monomers

with Organic Peroxides for the High Polymer Industry

Introduction

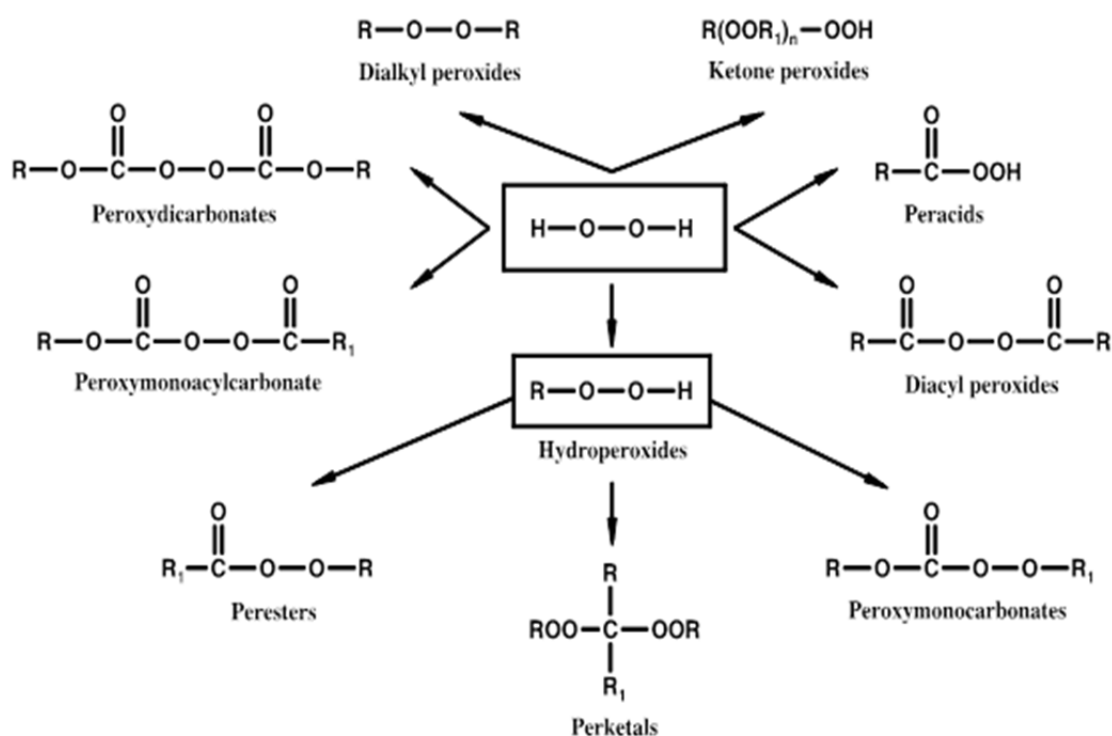
The polymerization of monomers is one of the main fields of application for organic peroxides. In this bulletin we would like to give you a rough overview on the use of organic peroxides for the free-radical polymerization. We will start off with a look at what qualifies organic peroxides for the polymerization of monomers followed by a look on the mechanism of the free radical polymerization. Next will be a short overview on the different types of polymerization processes for monomers. Finally we will take a closer look on the characteristics of the different organic peroxides which can be used for the free radical polymerization.

Initiators for high polymers

A wide range of organic peroxides and azo compounds are used as initiators for the radical polymerization of monomers. The reason for this is that organic peroxides are able to form radicals very easily by decaying of the O-O bond, induced by heat or by UV-radiation. This qualifies organic peroxides for a controllable trigger of the reaction and thus as an initiator for the free-radical polymerization. There are various types of organic peroxides available, which mainly differ in their thermal decomposition behavior. For this reason you can find organic peroxides for a broad temperature range.

Organic peroxides can be divided into diacylperoxides, hydroperoxides, dialkylperoxides, peroxyesters, peroxyketals and peroxy(di)carbonates (see Figure 1). The main areas of application for these initiators are the production of low density polyethylene (LDPE), polyvinylchloride (PVC), styrenics (PS/EPS), acrylics (PMMA) and other polymers. The polymerization of monomers takes place under varying controlled conditions, to which the properties of the initiator have to be adapted. Certain types of organic peroxides are also used for the chain degradation of polypropylene.

Figure 1: Types of Organic Peroxides



Free-Radical Polymerization

The synthesis of polymers is performed by linking of small molecules (*monomers*) in order to achieve macromolecules (*polymers*). Already during the 19th century this type of reaction was used in industrial scale, but only during the 20th century the researcher had understood the chemical background of this type of reaction and the age of the modern polymers was initiated.

The basic types of reaction are the polycondensation and the polyaddition.

The free-radical polymerization, which utilizes organic peroxides (Figure 1), but also Persulfates, compounds with an unstable C-C bond, Azo compounds and Hydrogen peroxide, is a polyaddition reaction, because the monomers react with each other without separation of byproducts.

A condition for this reaction will be that the reacting monomers are unsaturated compounds, i. e. compounds with a double bond between two C atoms, see reaction scheme in figure 2:

Legend for Table 2

Frozen
Cooled
Explosive law
Min. storage temp.
P=Powder/F=Flakes/G=Granules/K=Crystalline

With this legend you are able to determine which products have to be stored at temperatures below 0 degrees Celsius or refrigerated, as well as which products are subject to the explosives law. Furthermore it shows you which products are having a minimum storage temperature. The minimum storage temperatures are however not stated in table 2 and have to be taken from the technical data sheet of the product, which we can supply to you upon request. The last line of the legend is stating in which solid form the product is available. The four different forms are powder, flakes, granules or crystalline form.

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Polymerization of Ethylene (LDPE)

with Organic Peroxides

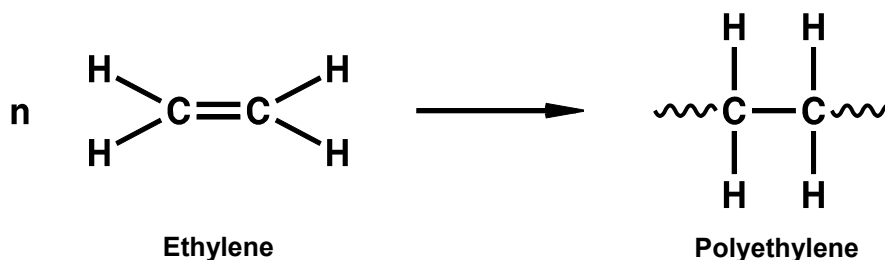
Introduction

Polyethylene is widely known and by far the most commonly used plastic. For its production also peroxides are utilized. This technical bulletin deals with the use of organic peroxide for the polymerization of Ethylene. It should give you a rough insight on the function of the processes for the production of Polyethylene (PE) and the available Peroxides that can be used for these processes. We will start off with a look at how polyethylene is formed and which different types of polyethylene can be distinguished. Next will be an overview for the two production processes. Finally we will take a look at which peroxides are suitable for the production of Polyethylene.

Polymerization of Ethylene

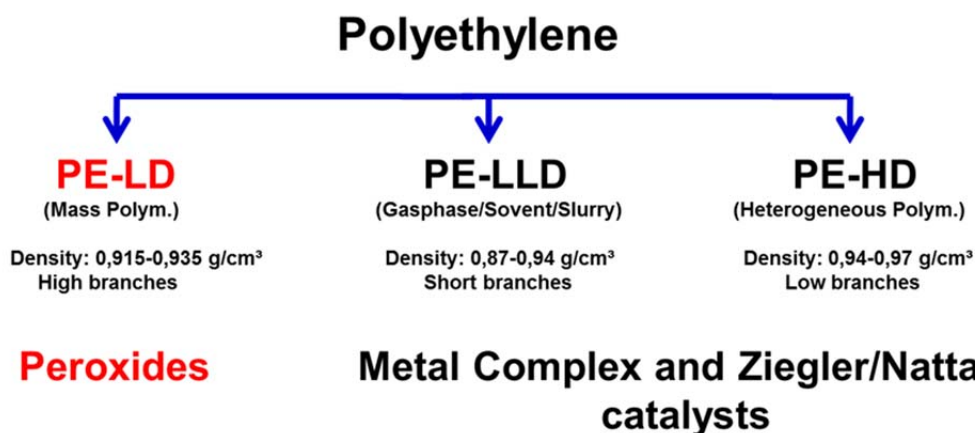
PE is a Thermoplastic and consists of very simple units (only Carbon and Hydrogen atoms, see figure 1).

Figure 1: Ethylene to Polyethylene



Depending on the polymerization processes one can distinguish between “two” groups of PE. Only Low Density Polyethylene (PE-LD) is produced with organic peroxides, while High Density Polyethylene (PE-HD) and Linear Low Density Polyethylene (PE-LLD) are produced with Metallocenes or Ziegler/ Natta catalyst (see figure 2).

Figure 2: Polyethylene Types



The industrial production of LDPE is known since 1936 (ICI process). It will be produced by a free-radical Polymerization at high pressures (1000 - 3000 bar). Besides the production process LDPE has also a different molecular structure (chain branching) and therefore a different density and crystalline structure. The final material is more flexible and transparent compared to HDPE.

Production Processes for LDPE

The free-radical Polymerization of Ethylene at high pressures to LDPE can be performed by two processes, either the tube reactor process or the autoclave process (figure 3).

Figure 3: Production Processes of LDPE

Autoclave (1300-2200 bar/155-320°C/Conversion 15-20%)
 or
Tube (O₂ or O₂+Peroxides) (2200-3000 bar/130-330°C/Conversion 15-30%)

A tube reactor (figure 4) consists of a high number of high pressure tubes; the total length of these tubes can be up to 2000 m. Repeated dosage of the initiator (organic peroxides or Oxygene) and fresh Ethylene will be performed at various segments of the tubes.

Figure 4: Tube Reactor

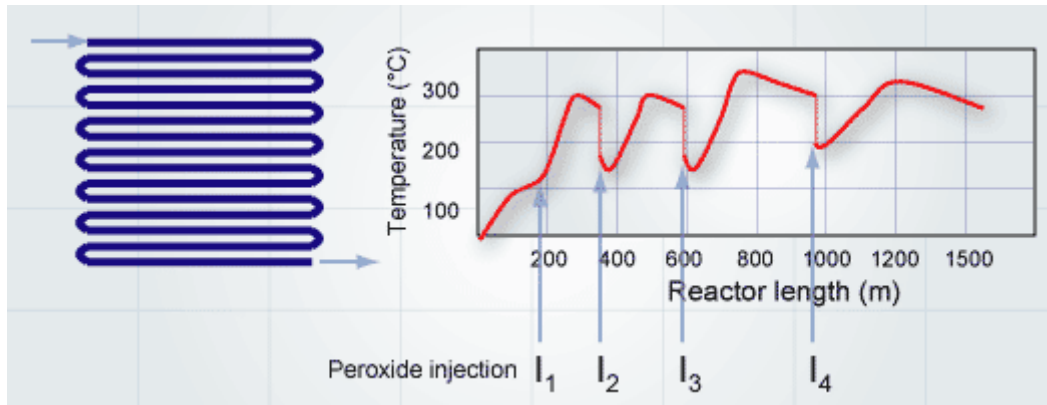
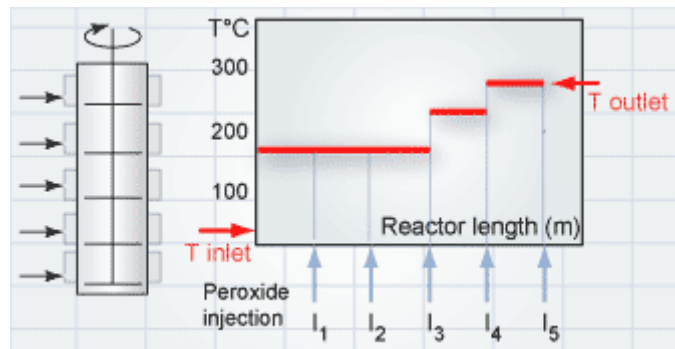


Figure 5: Autoclave



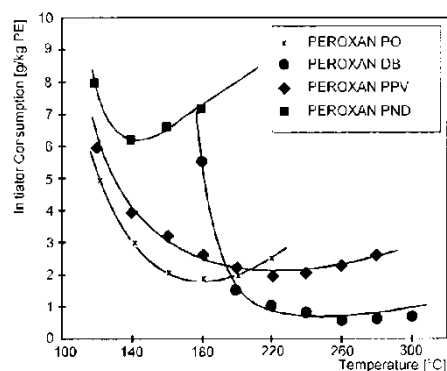
The size of an autoclave reactor (figure 5) is up to 2000 l. Multi-chamber types are often used. Repeated dosage of initiator and Ethylene will be performed in order to achieve a certain temperature profile in the reactor.

Both processes are bulk processes. The main criterion for the selection of a suitable initiator will be the polymerization temperature. In addition the physical properties of the LDPE, like degree of chain branching and therefore the density and crystalline structure are also determined by the polymerization temperature. The temperature profile ranges from approx. 130° C up to 330° C. At higher temperatures there is a risk of Ethylene decomposition; lower temperatures than 130° C can be not maintained due to the initiator activity and the low reactivity of the Ethylene. The typical reactor holding time of the Ethylene is about 1 min., the degree of conversion approx. 10 - 35 %. Due to the high viscosity of the LDPE one cannot obtain higher degrees of conversion.

Suitable Peroxides

The criterions for the peroxide selection are high polymerization activity and low consumption. From figure 6 it can be obtained that any type of peroxide does have a minimum consumption at a certain temperature.

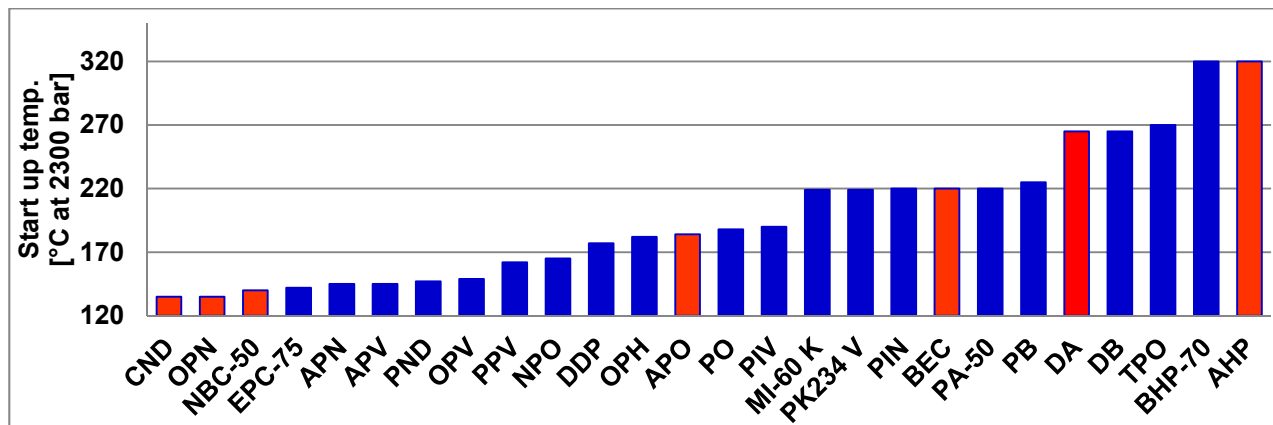
Figure 6: Polymerization of Ethylene; Peroxide Consumption for selected Peroxide as a Function of the Reaction Temperature



In addition the peroxide consumption is also influenced by the holding time and the pressure.

The peroxides (some of them are available in IBC quantities, too) must be pumped into the reactor at very high pressures, which may cause crystallization and decomposition of the peroxide. This can be avoided by utilizing diluted peroxide solutions or peroxides, which have a low tendency to crystallization (e. g. the tert.-Amyl equivalents of the tert.-Butyl peroxides). On this and the following page you will find peroxides of our product range that can be used for production of LDPE (figure 7 and table 1).

Figure 7: Organic Peroxides, utilized for Production of LDPE; Peroxides sorted on Descending Activity



Blue column: Food approval (BfR III)

Common Peroxides for low temperature area

PEROXAN...	Startup temp. [°C] at 2300 bar	Temp. range [°C]	Storage temp. [°C]	1 Hour half life temp. [°C]	SADT [°C]	Food approval (BfR III)
APN tert-Amyl peroxyneodecanoate	145	130-180	-25 to -15	61	20	Yes
APV tert-Amylperoxypivalate	145	130-180	-15 to -10	72	25	Yes
PND tert-Butyl peroxyneodecanoate	147	130-190	-30 to -10	64	15	Yes
OPV 1.1.3.3-Tetramethylbutylperoxy pivalate	149	150-200	<-15	66	20	Yes
PPV tert-Butyl peroxypivalate	162	150-200	-15 to -5	75	20	Yes
NPO Di-(3.5.5-trimethylhexanoyl)-peroxide	165	150-190	-8 to 0	77	20	Yes
OPH 1.1.3.3-Tetramethylbutyl peroxy-2-ethylhexanoate	182	150-210	<+5	88	35	Yes
PO tert-Butyl peroxy-2-ethylhexanoate	188	180-230	-30 to +15	91	35	Yes

Common Peroxides for medium temperature range						
PK234 V 2,2-Di-(tert.-butylperoxy)-butane	219	190-250	<+30	116	70	Yes
PIN tert-Butyl peroxy-3,5,5-trimethylhexanoate	220	210-240	-20 to +30	114	60	Yes
PB tert-Butyl peroxybenzoate	225	220-270	+10 to +30	122	60	Yes
Common Peroxides for high temperature range						
DA Di-tert-amyl peroxide	265	225-280	<+30	128	80	--
DB Di-tert-butyl peroxide	265	240-280	<+30	141	80	Yes

In case you should have any further questions please do not hesitate to contact us personally. We will be pleased to assist you.

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Degradation of Polypropylene (PP)

for controlled rheology CR-PP with Organic Peroxides

Introduction

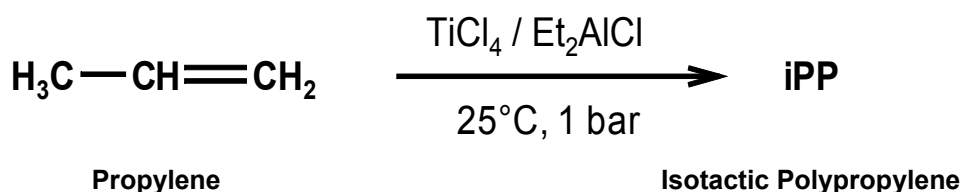
This technical bulletin deals with the use of organic peroxide for the degradation (visbreaking) of polypropylene (PP) for controlled rheology CR-PP. It should give the reader a rough insight on the function of this process and an overview of the available Peroxides that can be used.

Degradation of Polypropylene

PP is a high-quality thermoplastic polymer. The industrial production had started in 1957. In recent years PP has become a polymer of more and more out-standing importance. The demand and therefore the increase of PP production capacity are much higher compared with the other polymers.

Contrary to the polymers like LDPE, PVC or PS, the Polymerization of PP is not a free-radical induced reaction, i. e. a reaction which is started by initiators like organic peroxides. Utilization of stereospecific catalysts, like Ziegler-Natta catalysts (figure 1) or Metallocenes leads to polymerisates with a well-ordered spatial chain configuration. This configuration improves the properties of the final products with respect to final products with a disordered spatial chain configuration.

Figure 1: Propylene / Polypropylene



However during processing of high molecular weighted PP organic peroxides are often utilized. This is because degradation of the polymer chains by peroxides improves the flow properties of the PP at its melting range. Due to a selective chain degradation one achieves a narrower molar mass distribution, a slightly lower molar mass and a lower melting temperature. This effect is characterized by the *Melt Flow Index (MFI)*, which is the amount of PP, that flows out from a nozzle with certain dimensions during a period of 10 min. at a given temperature and load (e. g. MFI 190 / 2.16 means: MFI at 190° C and a load of 2.16 kg).

Due to its chemistry the degradation of PP is a special case of the peroxide induced crosslinking. Therefore the PP degradation is often handled as a subclass of this field of application.

The basic differences with respect to the peroxide induced, free-radical Polymerization reaction are:

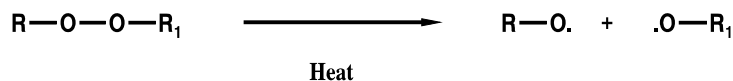
- The chain degradation is a stoichiometric reaction, but not a chain reaction. This means that for the scission of one chain one free-radical is needed.
- Suitable are only such types of peroxides, which decompose in high energy free-radicals. The amount of energy must be high enough to abstract a Hydrogen atom from the polymer chain.

In principle all polymers, which chains consist mainly of tertiary C atoms, like Polypropylene, Polybutylene and Polyvinylchloride, are degradable by peroxides. This also means that these polymers cannot be crosslinked. A crosslinking reaction is only possible, if the appropriate copolymerisates of the above mentioned polymers with Ethylene are used.

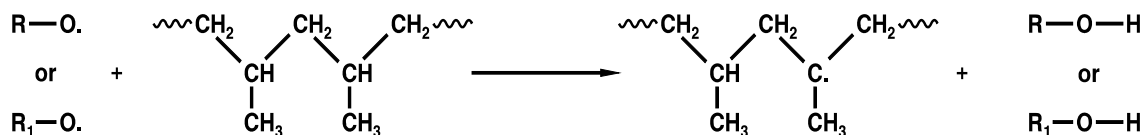
Regarding PP the free-radicals react mainly with the tertiary CH group, which leads to a chain scission at the β -position of the tertiary C atom under attack, the so-called β -Scission (Figure 2):

Figure 2: Mechanism of Degradation

1. Radical formation



2. Hydrogen abstraction



3. Degradation (beta-Scission)

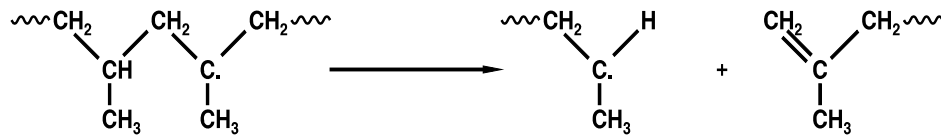
**Suitable Peroxides**

Table 1 shows a survey of organic peroxides, which are suitable for degradation of PP. From the peroxides listed in table 1 PEROXAN DB will be the cheapest and PEROXAN HX the most expensive alternative; PEROXAN BIB will be in the middle of the prior mentioned types. More important than the price is the equipment used by the customers:

- Usage of PEROXAN DB requires a closed system, due to its volatility.
- A dosage equipment for liquid peroxides can often be changed only to a system which is suitable for dosage of solid peroxides by time and money consuming construction.

Important parameters for the PP degradation are the reaction temperature and duration. For the selection of both parameters one has to take into consideration that the reaction duration must be equivalent to at least 10 times the half life time of the utilized peroxide at the reaction temperature. At lower reaction durations a partly degraded PP is obtained, which still contains non-decomposed peroxide. Figure 3 shows the influence of the peroxide dosage on the MFI of Polypropylene.

Figure 3: Influence of PEROXAN HX Dosage on the MFI of PP; Starting MFI of PP is 4, Reaction Temperature: 230° C, Duration of Reaction: 1.6 min.

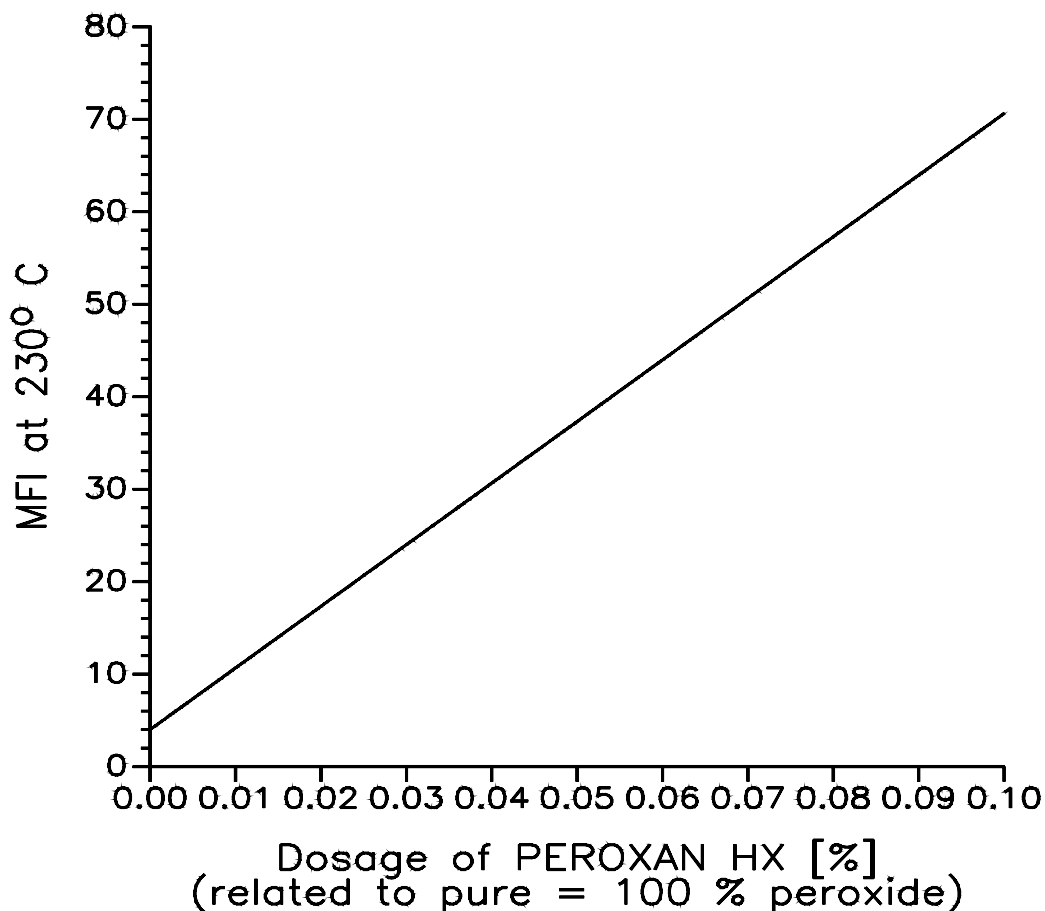


Table 1: Survey of Organic peroxides, suitable for degradation of PP

	PEROXAN...	SADT	HWZ [1 min.]	Food approval (BfR VII)	FDA [21 CFR ...]
tert.-Butyl peroxyisopropylcarbonate	BIC	60 °C	155 °C	Yes (0,5%)	--
Di-tert-amyl peroxide	DA	75 °C	169 °C	--	177.1520 (a)(1) 177.1520 a)(3)(i) (0,2%)
Di-(2-tert-butyl- peroxyisopropyl)-benzene	BIB and formulations	80 °C	174 °C	Yes (0,1%)	--
2.5-Dimethyl-2.5-di-(tert- butylperoxy)-hexane	HX and formulations	80 °C	174 °C	Yes (0,1%)	1771520 (c) TBA < 100 ppm
Di-tert-butyl peroxide	DB	80 °C	183 °C	Yes (0,1%)	--

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Polymerization of Vinyl chloride (PVC)

with Organic Peroxides

Introduction

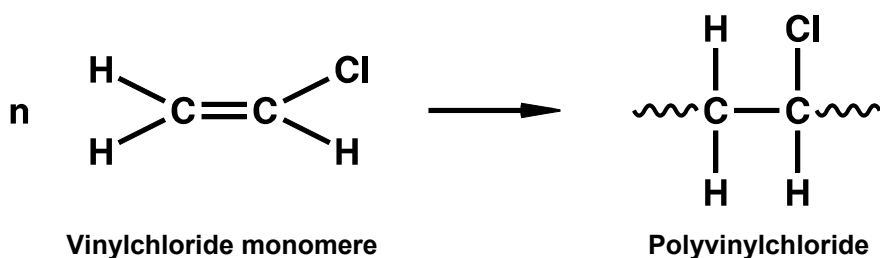
This technical bulletin deals with the use of organic peroxide for the polymerisation of Vinyl chloride. It should give the reader a rough insight on the function of the processes for the production of Polyvinylchloride (PVC) and the available Peroxides that can be used for these processes.

Polymerisation of Vinyl chloride (PVC)

PVC was discovered in 1835, but its industrial production was only started in 1928. With respect to production capacity PVC is at present one of the most important thermoplastics. PVC is characterized by a remarkable resistance, gas impermeability and a good resistance to light and weathering. The flammability is very low, PVC doesn't burn outside a flame.

PVC is produced from Vinyl chloride and, by adding peroxides, is polymerized to Polyvinylchloride (Figure 1).

Figure 1: Vinylchloride/ Polyvinylchloride

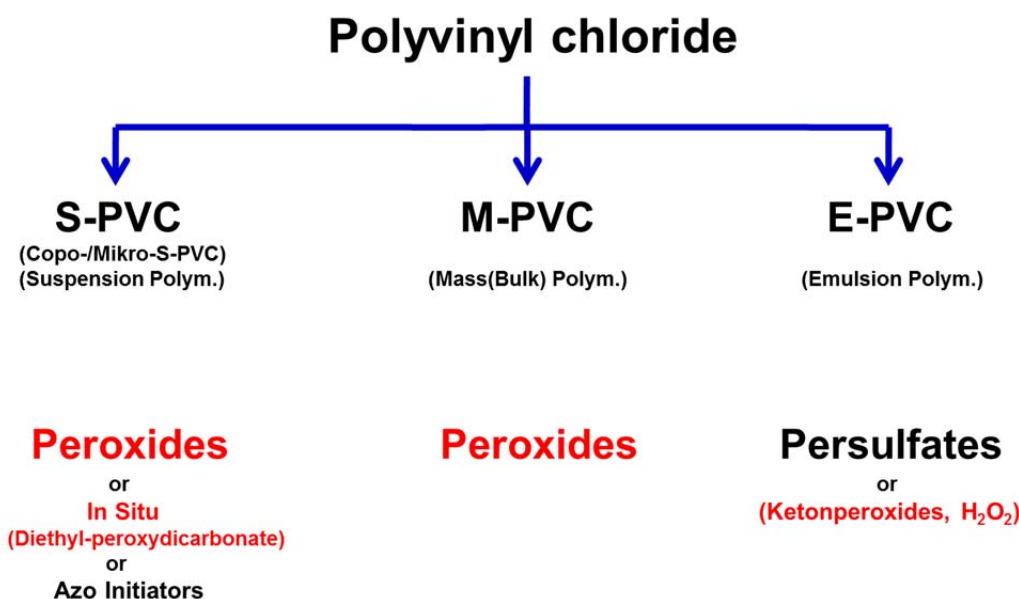


A serious problem during PVC production is the extremely high tendency of the Vinyl chloride to cause cancer (MAK value < 3 ppm¹). Vinyl chloride is a gas at ambient temperatures (boiling point: - 14° C) and is therefore polymerized in liquid phase under pressure. Due to its toxicity more and more producers perform the polymerisation reaction in closed reactor systems with dosage equipment for additives and initiators. To avoid any opening of the reactor for addition of initiators, these have to be in liquid phase to allow a dosage by a pump. These liquid-phase initiators have become more and more important during the last years.

Production Processes

In principle one can differentiate between three production processes used for polymerisation of Vinyl chloride (Figure 2).

Figure 2: Polyvinylchloride Types

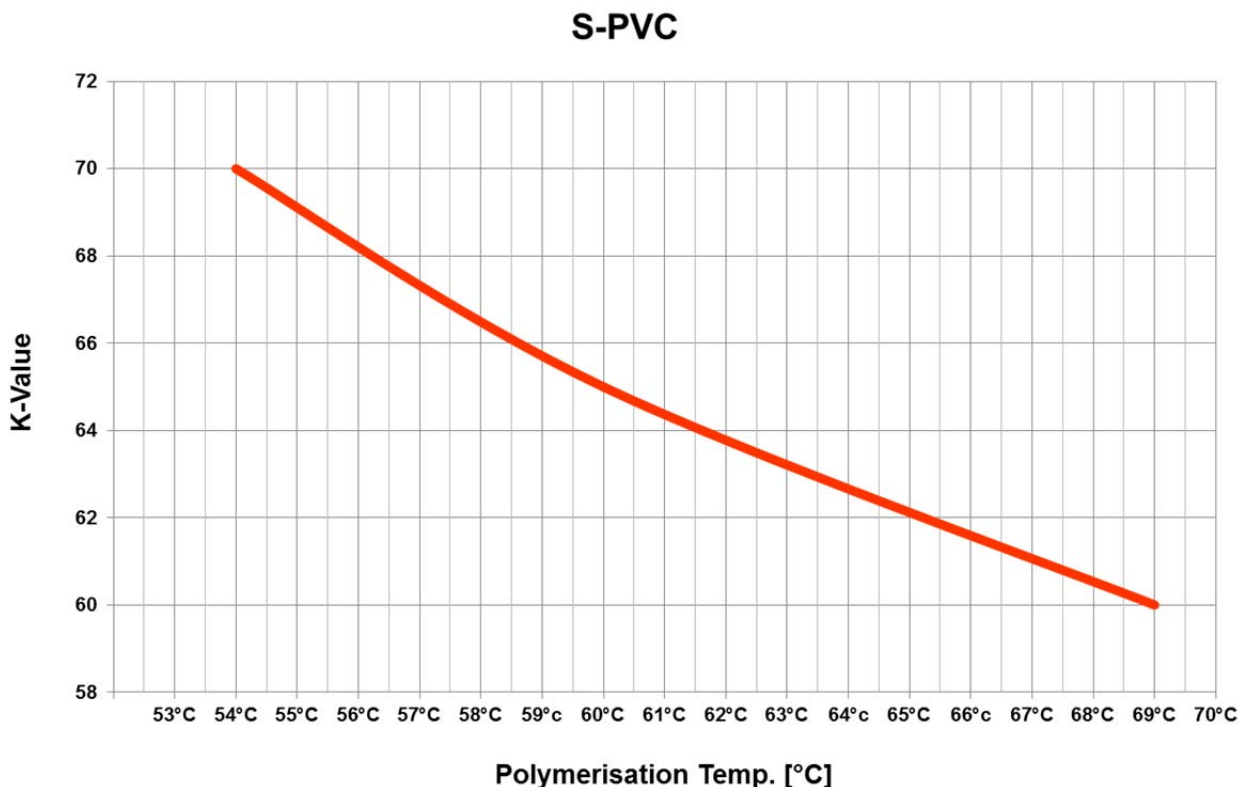


¹ <http://www.dguv.de/ifa/Fachinfos/Occupational-exposure-limit-values/Verbindliche-Arbeitsplatzgrenzwerte-der-EU-Kommission/index.jsp>, 17.05.2016

The share of S-PVC with respect to the total PVC reads 80 %. For the S- and M-PVC production organic peroxides (Diacyl peroxides, Peroxydi-carbonates and Peresters) are utilized exclusively. For the E-PVC production water soluble initiators, like Persulfates, Hydro peroxides and Ketone peroxides are used. Besides the production process the physical properties of the final product are depending solely on the molar mass of the PVC. Further the molar mass is nearly exclusively determined by the polymerisation temperature, but *not* by the type and/or concentration of the initiator. This effect occurs because, not the free-radicals of the peroxide, but Vinyl chloride radicals act as starter for the growth reaction of the polymer chain.

Figure 3 shows the molar mass - expressed in terms of the so-called K-value by Fikentscher (DIN EN ISO1628-1) - as a function of the Polymerisation temperature. It can be seen that the molar mass decreases with increasing Polymerisation temperature. As a consequence one has to utilize peroxides with a high reactivity at low temperatures in order to produce PVC of high K-values.

Figure 3: Molar Mass of S-PVC



Suspension Polymerisation (S-PVC)

The suspension polymerisation is a batch process. In an autoclave reactor the raw materials water, Vinyl chloride, suspending agents and initiator are stirred in order to achieve dispersion. Depending on the molar mass that wants to be achieved the polymerisation will be performed at temperatures between 40° C and 70 ° C and a pressure between 8 and 12 bar (also see figure 3).

Suitable Peroxides for S-PVC

Exclusively monomer soluble peroxides are used, ranging from liquid, high active products, like PEROXAN CND and PEROXAN EPC, to the solid Peroxydicarbonates, like PEROXAN BCC, C124 and C126, which have a reasonable storage life at moderate temperatures, and also PEROXAN LP.

To achieve a regular course of the reaction during the whole polymerisation reaction - which can take up to 10 hours -, combinations of different peroxides are often used. Common combinations are Peroxydicarbonates, like PEROXAN EPC, PEROXAN BCC, PEROXAN C124 or PEROXAN C126 with Dilauroyl peroxide (PEROXAN LP) or Azo compounds (PEROXAN AZDN). Figure 4 and 5 show the degree of Vinyl chloride conversion for several peroxides at a given temperature as a function of the duration of the polymerisation reaction.

Figure 4: Degree of Vinyl chloride Conversion at 45°C

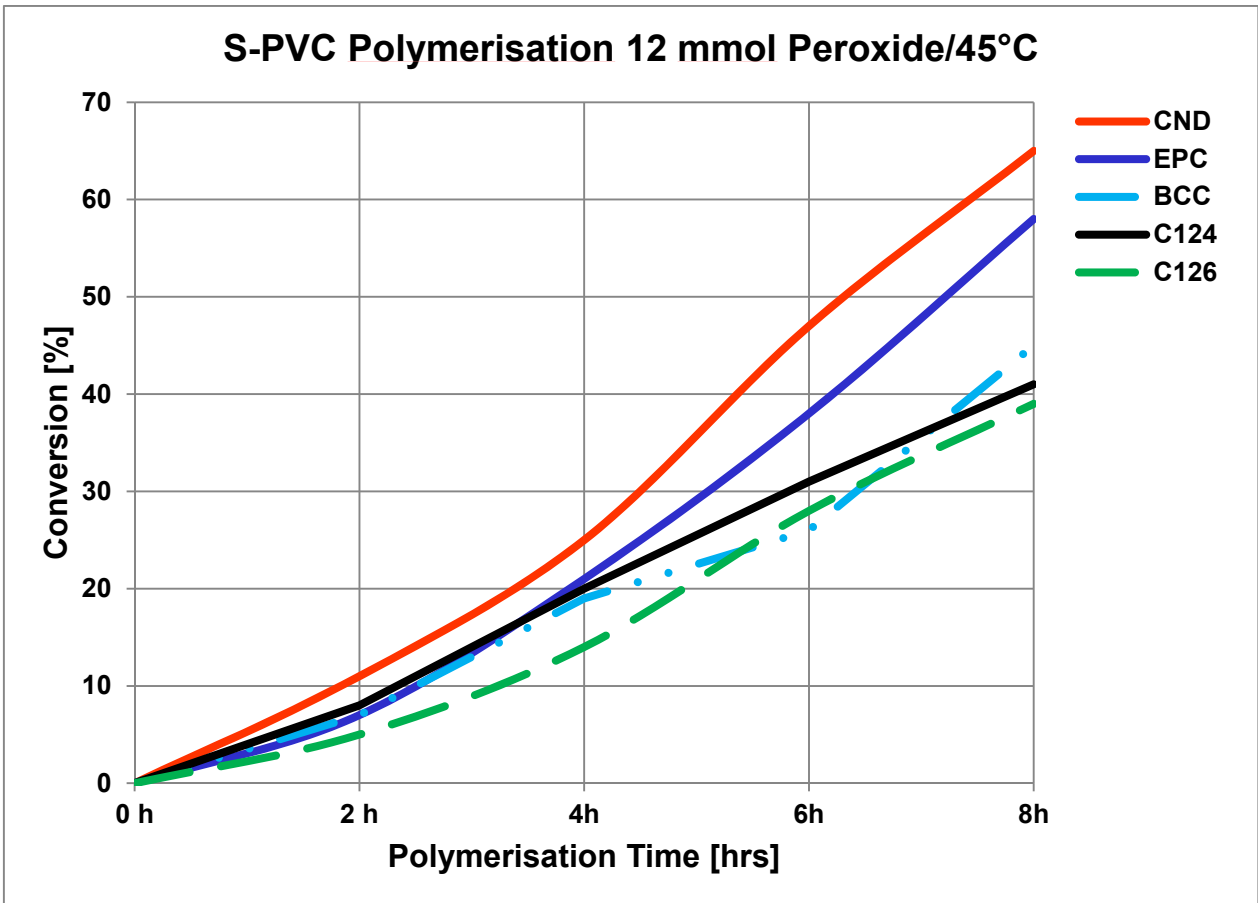
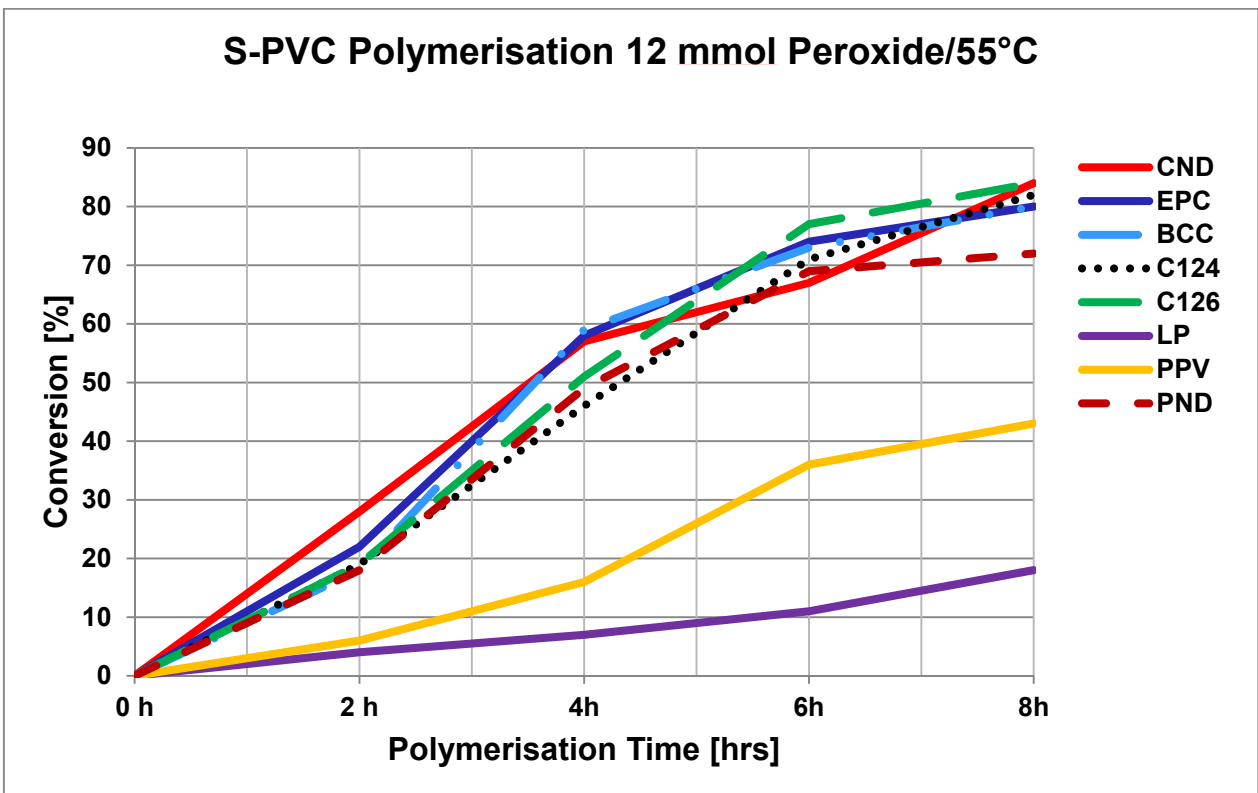


Figure 5: Degree of Vinyl chloride Conversion at 55°C



The above mentioned solid types of organic peroxides do not fulfil the request for initiators, which can be dosed in a liquid form, due to the toxicity of Vinyl chloride as well as the general request for the availability of an automated dosage equipment. Following this request water-based suspensions of the peroxides

PEROXAN BCC, PEROXAN C124 and PEROXAN LP were developed, which can be pumped (the viscosity ranges from 200 to 1000 mPas). The peroxide concentration reads 35 % for PEROXAN C124-35 W and 40 % for PEROXAN BCC-40 W, and PEROXAN LP-40 W. Because of the lower concentration these water-based suspensions allow a much safer handling compared with the technically pure products. The suspensions are incombustible, the total dissipated energy resulting from a peroxide decomposition isn't high enough to vaporize the complete amount of water of the suspensions. Besides peroxide and water the suspensions consist of thickening agents and emulsifiers (total maximum concentration = 1 - 2 %). In contrast to the chemical stability of the peroxide itself - the storage life without loss in activity (6 months and even longer if the recommended storage temperature is maintained) - the physical stability of the suspensions is limited to 3 months. A longer period of storage time will lead to sedimentation of the suspension's solid. But this sedimentation is a reversible process, because the suspension can be re-homogenized by stirring. If the suspensions are stored at temperatures of 30° C and above, thixotropy (increase in viscosity by several powers) will occur, which is an irreversible process. Transport and storage in 900 kg IBCs will be an additional advantage of the suspensions. This allows an easy set-up for an automated dosage equipment, because the suspensions can be pumped directly from the IBCs.

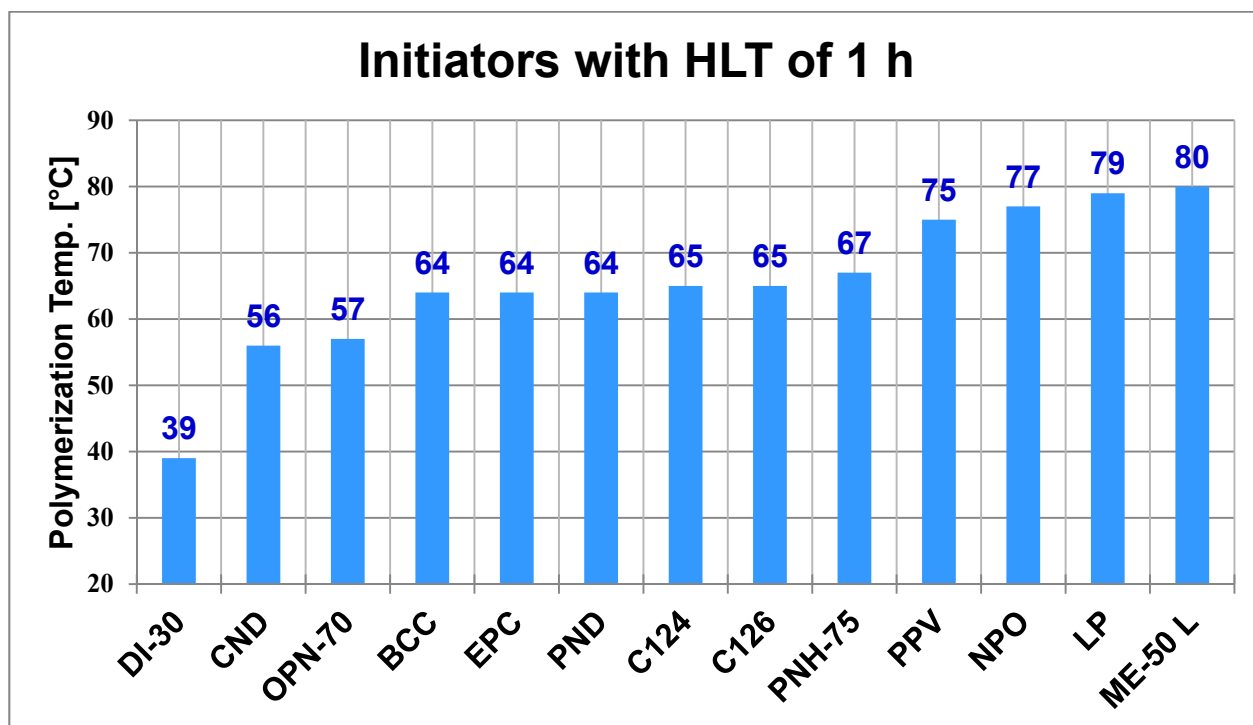
Bulk or Mass Polymerisation (M-PVC)

The bulk polymerisation is a batch process, which is performed in two stages, due to the complicated dissipation of heat, generated during the exothermic polymerisation reaction. Both stages are performed in autoclave reactors. During the first stage a 10 % degree of Vinyl chloride conversion will be reached. The main polymerisation is performed in the second stage by adding a different type of peroxide. For this process the reaction temperatures are between 50° C and 70° C, at pressures between 8 and 16 bar.

Suitable Peroxides for M-PVC

In the first stage usually peroxides of high activity like PEROXAN CND are utilized. The main polymerisation is initiated by Peroxydicarbonates (PEROXAN EPC, PEROXAN BCC, PEROXAN C124 or PEROXAN C126). In figure 6 you will find a range of organic peroxides with plotted against the polymerisation temperature.

Figure 6: Initiators with HLT of 1h



No food approval (BfR II) for PVC

Survey of Organic Peroxides for the Suspension and Bulk Polymerisation of Vinyl chloride

Below you will find a survey on a selection of organic peroxides that can be used for the Suspension and Bulk Polymerisation.

Cumylperoxy neodecanoate	
PEROXAN CND	75 %, Solution in Isododecane
PEROXAN CND-50 WN-A	50 %, non-freezing Emulsion in water with methanol
Suitable for Suspension / Bulk Polymerisation (PEROXAN CND) at 35° C to 45° C. Already active at low temperatures, therefore suitable for PVC with high molar mass (high K-values) and also to shorten the induction period of Polymerisation reaction. (Alternative of Acetylcyclohexane sulfonyl peroxide.)	
Di-(2-ethylhexyl) peroxydicarbonate	
PEROXAN EPC-65/75	65/75 %, Solution in Isododecane
PEROXAN EPC-50/60 WN-A	50/60 %, non-freezing Emulsion in water with methanol
Suitable for Suspension / Bulk Polymerisation (PEROXAN EPC-75 (65)) at 45° C to 60° C. Avoids fouling on the inner surface of the reactor. PEROXAN EPC 50/60 WN-A: safe handling, due to water as phlegmatizer.	
Di-(4-tert.-butyl cyclohexyl) peroxydicarbonate	
PEROXAN BCC	95 %, Powder
PEROXAN BCC-75	75 %, water-wet Powder
PEROXAN BCC 40-W	40 %, water-based Suspension
Suitable for Suspension / Bulk Polymerisation (PEROXAN BCC, PEROXAN BCC-75) at 45° C to 60° C. Avoids formation of pin holes / fish eyes in the PVC and scab formation in the reactor. The technically pure powder has a reasonable high activity and in addition a long storage life at + 15° C. The water-wet powder PEROXAN BCC-75 is safer to handle (25 % water as phlegmatizer). PEROXAN BCC 40-W, the water-based suspension can be pumped and is therefore suitable for automatic dosage equipment. Due to the high water content (60 %) very safe to handle. Transport and storage in IBCs is possible.	
Dicetyl peroxydicarbonate	
PEROXAN C124	95 %, Powder
PEROXAN C124 35-W	35 %, water-based Suspension
Suitable for Suspension / Bulk Polymerisation (PEROXAN C124) at 45° C to 60° C. Avoids formation of pin holes / fish eyes in the PVC and scab formation in the reactor. PEROXAN C124 40-W can be pumped and is suitable for automatic dosage equipment. Due to the high water content (60 %) very safe to handle. Transport and storage in IBCs is possible.	
Dimyristyl peroxydicarbonate	
PEROXAN C126	95 %, Powder
Suitable for Suspension / Bulk Polymerisation (PEROXAN C126) at 45° C to 60° C. Avoids formation of pin holes / fish eyes in the PVC and scab formation in the reactor..	
tert.-Butyl peroxyneodecanoate	
PEROXAN PND	95 %, Liquid
PEROXAN PND-75	75 %, Solution in Isododecane
PEROXAN PND-50 WN-A	50 %, non freezing emulsion in water with methanol
Suitable for Suspension / Bulk Polymerisation (PEROXAN PND, PEROXAN PND-75) at 50° C to 65° C. Lower oxidizing; more active than PEROXAN PPV. Liquid products therefore suitable for automatic dosage equipment. PEROXAN PND: technically pure product, contains no phlegmatizer. PEROXAN PND-50 WN-A: safe handling, due to water as phlegmatizer. (Alternative of 2.2'-Azo-di-(2.4-dimethylvaleronitrile).)	
tert.-Butyl peroxyvalate	
PEROXAN PPV-65/75	65/75 %, Solution in Isododecane
Suitable for Suspension / Bulk Polymerisation at 50° C to 65° C. Lower oxidizing. Liquid products, therefore suitable for automatic dosage equipment.	
Dilauroyl peroxide	
PEROXAN LP	98 %, Powder
PEROXAN LP 40-W	40 %, water-based Suspension
Suitable for Suspension / Bulk Polymerisation (PEROXAN LP) at 50° C to 70° C. In combination with more active peroxides a regular course of Polymerisation up to the end of reaction is obtained. PEROXAN LP is suitable for the copolymerisation of Vinyl chloride and Vinyl acetate. PEROXAN LP 40-W can be pumped and is suitable for automatic dosage equipment. Due to the high water content (60 %, resp. 75 %) very safe to handle. Transport and storage in IBCs is possible. (Alternative of PEROXAN AZDN (2.2'-Azo-diisobutyronitrile).)	

Due to the properties the following peroxides are also suitable for the Polymerisation of Vinyl chloride, but in practical not used:

PEROXAN NBC-50	Di-n-butyl peroxydicarbonate (equivalent to the a. m. Peroxy dicarbonates)
PEROXAN NPO	Di-(3,5,5-trimethyl hexanoyl) peroxide (lower activity compared with PEROXAN PPV)

Emulsion Polymerisation (E-PVC)

The emulsion polymerisation is also performed in an autoclave reactor at temperatures of 40° C up to 75° C; the pressure corresponds to the saturation pressure of the Vinyl chloride at these temperatures. The emulsion polymerisation can also be designed as a continuous process. The Vinyl chloride, water and emulsifier are dispersed by stirring. Water-soluble per-compounds (like Persulfates or Hydro peroxides) as well as water-soluble Ketone peroxides are utilized as initiators. Because these above mentioned initiators are relatively inactive at the prior mentioned temperatures, the usage of redox systems (like peroxide / Ascorbic acid / Iron salts) are common in order to achieve the appropriate free-radical concentration.

Micro Suspension Polymerisation (Micro-S-PVC)

Micro-S-PVC has already replaced the E-PVC for most applications. The production process is very similar to the one for the suspension polymerisation. The compounds water, vinyl chloride, emulsifier and monomer soluble initiator are homogenized thoroughly, in order to achieve a suspension with a very low droplet size. The Polymerisation is also performed in an autoclave reactor. Suitable initiators are water-based suspensions of Peroxydicarbonates in combination with Dilauroyl peroxide suspension, i. e. PEROXAN BCC 40-W, PEROXAN C124 40-W in combination with PEROXAN LP 40-W.

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Polymerization of Styrene (PS)

with Organic Peroxides

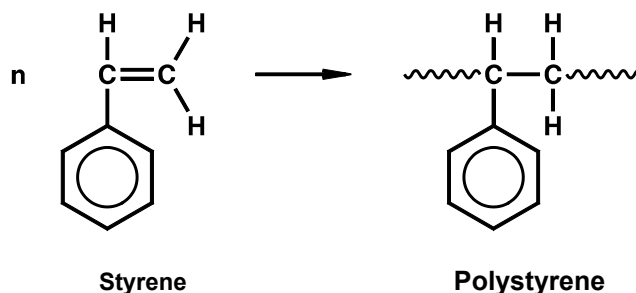
Introduction

This technical bulletin deals with the use of organic peroxide for the polymerisation of styrene. It should give you a rough insight on the function of the processes for the production of polystyrene (PS) and the available Peroxides that can be used for these processes.

Polymerisation of Styrene (PS)

PS was discovered in 1839, while the industrial production started in 1931. It is formed by a free-radical polymerisation from styrene (see figure 1). With respect to production capacity PS and its copolymers ranks at fourth position (after LDPE, PP and PVC).

Figure 1: Styrene/ Polystyrene

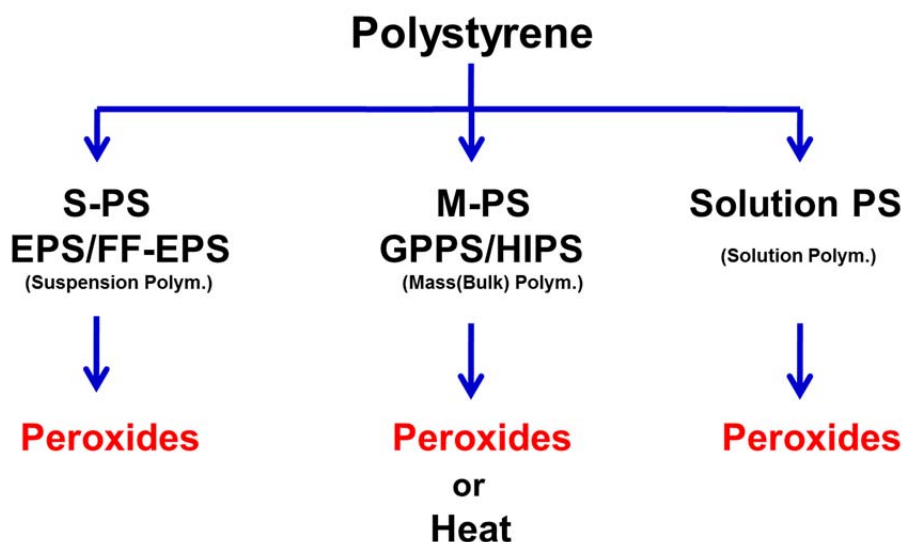


PS is crystal-clear, tough and brittle. It is characterized by a brilliant surface gloss and out-standing dielectric properties, but also by a tendency of stress crack formation and a low heat, weathering and solvent resistance. These negative properties can be eliminated by Copolymerisation with other Monomers (like Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$), Acrylonitrile ($\text{CH}_2=\text{CH}-\text{CN}$)). Applications of PS are for example production of cases, packaging and foams for insulation applications.

Production Processes

PS is produced by 3 different processes (see figure 2), namely suspension, bulk and solution polymerisation. For all processes peroxides are utilized as initiators. However the bulk process can also be initiated by heat, i. e. without any initiators.

Figure 2: Polystyrene Types



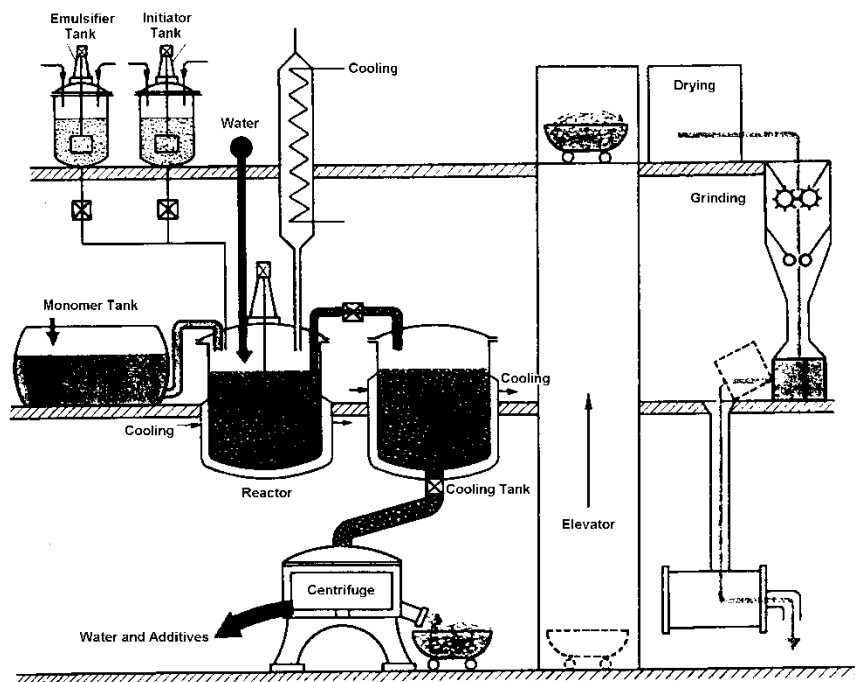
The properties of the final PS, like the molar mass, are depending on the process, but also on the temperature profile during the Polymerisation reaction and the type of peroxides (free-radicals of the peroxide and not monomer radicals act as starters for the growth reaction of the polymer chain; different to PVC polymerisation).

Suspension Polymerisation (S-PS)

The suspension polymerisation (Figure 3) is a batch process. This process allows for a good heat dissipation, an easy control of the particle size of the final product and also a simple preparation of the final

PS. The raw materials (water, Styrene, suspending agent and initiators) are dispersed in a reactor. The Polymerisation reaction will be performed following a certain temperature profile to achieve the required molar mass of the PS.

Figure 3: Production process S-PS



Source: Kunststoffe – kurz und bündig, Karlheinz Biederbick, Vogel-Verlag, 4. Auflage 1977, S.65

Suitable Peroxides

The "classical" process utilizes a combination of Dibenzoyl peroxide (PEROXAN BP-25 WD) and tert.-Butyl peroxybenzoate (PEROXAN PB) at a ratio of 3:1. However the decomposition products of both above mentioned peroxides will contain aromatic compounds. As the main part of the PS production will be consumed in food packaging industry, all Western European producers have signed a self-obligation to, for the future, only produce such types of PS, which show a very low remaining content of aromatic compounds. This self-obligation is implemented in two steps:

- In a first step the PEROXAN PB will be replaced by a peroxide with an equivalent half life time, but without any aromatic decomposition products. This peroxide, the tert.-Butyl peroxy 2-ethylhexylcarbonate (PEROXAN BEC), a Peroxymonocarbonate ester, has - besides the advantage of non-aromatic decomposition products - also a much higher activity. By this the remaining styrene content of the final PS, which is also an aromatic compound, can be decreased by several powers compared to the use of PEROXAN PB.
- In a second step also the Dibenzoyl peroxide can be replaced by a non-aromatic equivalent, the tert.-Butyl peroxy 2-ethylhexanoate (PEROXAN PO).

Table 1 shows a survey of peroxides and their advantages, which are common for the suspension polymerisation of Styrene. In Table 2 the reader will find a choice of standard recipes.

Table 1: Overview of peroxides and their advantages

Product Name / Chemical Name	Half Life Temperature [° C]			Degree of Conversion [%] (1 mmol / 100 grs Styrene)		Remarks
	10 h	1 h	1 min.	4 h / 90° C	2 h / 130° C	
PEROXAN BP-25 WD Dibenzoyl peroxide	72	92	130	65	---	Standard Decomposition products: CO ₂ , Benzene, Diphenyl, Benzoic acid, Phenyl benzoate
PEROXAN PO tert.-Butyl peroxy 2-ethyl-hexanoate (alternatively PEROXAN APO , tert.-Amylperoxy 2-ethyl-hexanoate can be utilized)	74	93	133	58	---	Non-aromatic alternative of PEROXAN BP-25 WD Decomposition products: CO ₂ , Methane, Ethane, n-Heptane, 5,6-Diethyldecane, Acetone, tert.- Butanol, 2-Ethylhexanoic acid

PEROXAN PB tert.-Butyl peroxybenzoate	106	125	168	16	80	Standard Decomposition products: CO ₂ , Methane, Ethane, Acetone, tert.-Butanol, Benzene, Benzoic acid, Diphenyl
PEROXAN BEC tert.-Butylperoxy-2-ethylhexylcarbonate	100	121	166	25	80	Non-aromatic alternative of PEROXAN PB Decomposition products: CO ₂ , tert.-Butanol, 2-Ethylhexanol
PEROXAN BIC tert.-Butyl peroxyisopropylcarbonate	99	118	159	---	---	Also non-aromatic, but more active than PEROXAN BEC Decomposition products: CO ₂ , tert.-Butanol, Isopropanol
PEROXAN PK-122 1,1-Di-(tert.-butyl peroxy)-cyclohexane	97	116	155	40	> 80	Graft Polymerisation

Table 2: Standard recipes

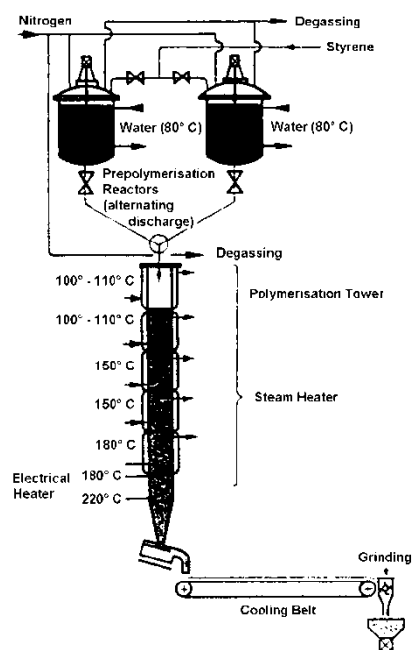
Polystyrene-Type	GP-PS	E-PS	FF-EPS
Dosages	w/w-%	w/w-%	w/w-%
Dibenzoyl peroxide	0,30	0,3	0,3
tert.-Butylperoxy benzoate	0,09		
tert.-Butyl-peroxy-2-ethylhexylcarbonate		0,11	
Dicumylperoxide			0,6
Pentane		8	8
Hexabromo cyclododecan (HBCD)	0,67		0,4
Temp.-Profile	4h/89°C -->3h/130°C	4h/89°C -->3h/130°C	4h/89°C -->3h/140°C

GP = General purpose- / E = Expandable- / FF = Flame retardant-PS

Bulk Polymerisation (M-PS)

The Bulk polymerisation (see figure 4) is a two stages process, often initiated by the influence of heat, but also by organic peroxides as listed in table 1.

Figure 4: Production process M-PS



Source: Kunststoffe – kurz und bündig, Karlheinz Biederbick, Vogel-Verlag, 4. Auflage 1977, S.57

A well-known problem of this process is the dissipation of reaction heat as well as the increasing viscosity of the reaction mixture during polymerisation. The final PS obtained from this process has a very low content of contaminations, but the necessary technical equipment is complicated and expensive. A pre-polymerisation up to a degree of Styrene conversion of 35 % is performed in an autoclave reactor with stirring facilities at a polymerisation temperature of 80° C. This pre-polymerisate is transferred to a tower reactor. Here the Polymerisation reaction is continued at several temperature levels, ranging from 110° C up to 220° C. The graft polymerisation of Polybutadiene on Styrene - to achieve shock-proofed PS - is performed by the same process.

Solution Polymerisation (L-PS)

This process is performed in sequential-connected reactors, at the temperature range from 80° C to 240° C. Equivalent to the suspension polymerisation also during the solution polymerisation the reaction heat can easily be removed over the solvent (e. g. Ethylbenzene). However the preparation of the polymerisate is costly, due to the necessary evaporation of the solvent from the final PS. Besides the peroxides listed in Table 2 also peroxides with higher half life time can be utilized, due to the high polymerisation temperature (up to 240° C) in this process.

Expanded Polystyrene (EPS)

EPS can be produced by a suspension as well as a bulk process. In case of suspension polymerisation the blowing agent (e. g. Pentane) can be added during the polymerisation reaction. In case of a bulk process the blowing agent has to be added after the Polymerisation reaction in a second manufacturing step, utilizing an extruder.

Copolymerisates of Styrene

The common copolymerisates of Styrene are shown in Table. 3.

SBR (Styrene-Butadiene-Rubber)	Copolymerisate consisting of approx. 30 % Styrene and 70 % Butadiene. Common production process is the so-called "Cold Polymerisation".
SB (Shock-proofed Polystyrene)	Graft Polymerisation of Styrene on Polybutadiene in Emulsion.
SAN (Styrene-Acrylonitrile)	Copolymerisate consisting of approx. 30 % Styrene and 70 % Acrylonitrile. Production by either Solution, Suspension or Precipitation Polymerisation.
ABS (Acrylonitrile-Butadiene-Styrene)	Graft Polymerisation of Styrene and Acrylonitrile on Polybutadiene in Emulsion.

Nearly all of the above mentioned copolymerisates (exception: SAN) are produced by emulsion polymerisation. Therefore water-soluble initiators like Persulfates or Hydroperoxides (e. g. tert.-Butyl hydroperoxide (PEROXAN BHP-70), Cumene hydroperoxide (PEROXAN CU-80 L) or Diisopropylbenzene monohydroperoxide (PEROXAN IHP-50)) are utilized. Due to the low activity of the Hydroperoxides at the typical reaction temperatures of the emulsion polymerisation, the use of redox systems, like Hydroperoxide / Dextrose / Iron salts, is common.

Flame Retardants/Synergists

Flame resistance of polymers which are utilized for construction and electrical industry is a necessary requirement. Polymers with flame retardants are PS (expandable PS, shock-proofed PS and copolymers of PS), but also Polypropylene (PP).

A flame retardant consists of two compounds, the real flame retardant (e. g. Hexabromo-cyclododecane) and a compound which decomposes in free-radicals. Mainly Dicumyl peroxide (PEROXAN DC) or 2.3-Dimethyl-2.3-diphenylbutane (PERGASAFE FR) is utilized. In case of fire, i. e. high temperatures the peroxide decomposes in free-radicals, which liberate the Bromine from the Hexabromo-cyclododecane and the fire will be extinguished. PEROXAN DC can already be added during the PS Polymerisation, because it doesn't disturb the reaction. The Bromine compound must be added after the polymerisation. PERGASAFE FR can be used in the extrusion process of EPS, too.

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