LUPEROX®
Organic Peroxides

Luperox® JWEB50: An initiator for higher molecular weight PS and improved productivity

Introduction

Arkema is pleased to introduce a novel multi-functional initiator: Luperox® JWEB50. We have developed this initiator specifically for the styrenics industry to produce high molecular weight, high-heat, crystal PS at improved productivity in a cost effective manner.

Luperox® JWEB50 is a room temperature stable, liquid peroxide with a half-life similar to currently used cyclic perketals and is appropriate for use in mass PS processes.

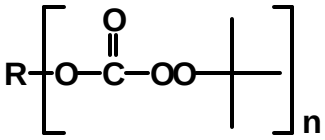
FEATURES

High MW at Equivalent Productivity

Luperox® JWEB50 can be used alone or in combination with a cyclic perketal (e.g. Luperox® 331M80) to provide higher molecular weight resin than that obtainable from a di-functional initiator alone. Table 1 compares the molecular weights of resins produced in batch mode using a linear temperature ramp from 103 to 151ºC and a constant, total active oxygen (A[O]) comprising various ratios of Luperox® JWEB50 and Luperox® 331M80. Luperox® JWEB50 alone increases M_w by 35%. Note also that Luperox® JWEB50 is expected to slightly increase the polydispersity index (PDI) as a result of the high molecular weight fraction produced by the multi-functional initiator fragment.

Arkema Organic Peroxides operates a continuous mass polymerization unit composed of a continuous stirred tank reactor (CSTR) followed by a pseudo-plug flow reactor (PFR) capable of producing approximately 2 lbs/hr of PS. Table 2 compares Luperox® JWEB50 to Luperox® 331M80 at equivalent conditions. Here, Luperox® JWEB50 increases M_w by 21% at equivalent throughput.

Luperox® JWEB50



A[O] = 3.32 - 3.45 wt%
50 % assay in ethylbenzene
1 hr $T_{1/2}$ = 119ºC (in ethylbenzene)
? 121ºC (in dodecane)

Table 1. Batch polymerization; Luperox® JWEB50 and 331M80 at equivalent A[O].

wt%		M_n	M_w	PDI
JWEB 50	331M80			
0	100	141,000	325,000	2.3
20	80	146,000	336,000	2.3
60	40	150,000	375,000	2.5
100	0	169,000	440,000	2.6

5 hr reaction, linear temperature ramp from 103 to 151ºC

Table 2. Continuous polymerization; Luperox®JWEB50 and 331M80 at equivalent A[O].

Initiator	Mw	PDI	Production (lb/hr)
331M80	199,000	2.3	1.61
JWEB50	241,000	2.4	1.63

A[O] = 26.5 ppm; CSTR: res.time – 1h33m, T=119ºC for 331 and 123ºC for JWEB; PFR: 42m, T = 131-150ºC; Feed rate = 2.6 lb/hr

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Improved Productivity at Equivalent Mw

If one is capable of producing a higher molecular weight resin, the molecular weight can be sacrificed for improved productivity. In Table 3 we compare Luperox® 331M80, Luperox® JWEB50, and the blend of the two in a batch polymerization. Note that a relatively small proportion of Luperox® JWEB50 is needed for a 20% improvement in productivity. This result and model calculations suggest that as much as a 50% improvement in productivity is possible with higher concentrations of Luperox® JWEB50.

Shown in Table 4 are related results from our continuous unit, which show that resin molecular weight is relatively insensitive to changes in initiator concentration. Thus, production rate was increased by 26% with no significant loss in molecular weight. This should be compared to the behavior of mono- or di-functional initiators where an increase in initiator concentration, which is required for higher production rates, significantly decreases molecular weight.

Long-chain branched PS

A unique aspect of Luperox® JWEB50 is its ability to produce long-chain branching. Changes in melt rheology caused by branches have been used in polyolefins and even PET to improve processing behavior. As shown in Table 5 branching increases low shear viscosity and causes an earlier onset of shear thinning that results in a nearly equivalent high shear viscosity.

More interestingly, as shown in Figure 1, long chain branching increases the extensional viscosity and melt strength of PS. These features are useful in processing operations that require significant stretching.

Table 3. Batch polymerization illustrating productivity improvements.

Initiator	A[O] (ppm)	M_w	PDI	Rxn. time (hr)
331M80	23.1	340,000	85	5
JWEB50	23.1	419,000	85	5
331M80 JWEB50	18 8.5	344,000	82	4

Linear temperature ramp from 103 to 151ºC

Table 4. Continuous process with Luperox® JWEB50. Little loss in Mw at high [I], which is necessary for high productivity.

A[O] (ppm)	M_w	Production (lb/hr)
20.9	243,000	1.29
26.5	241,000	1.63

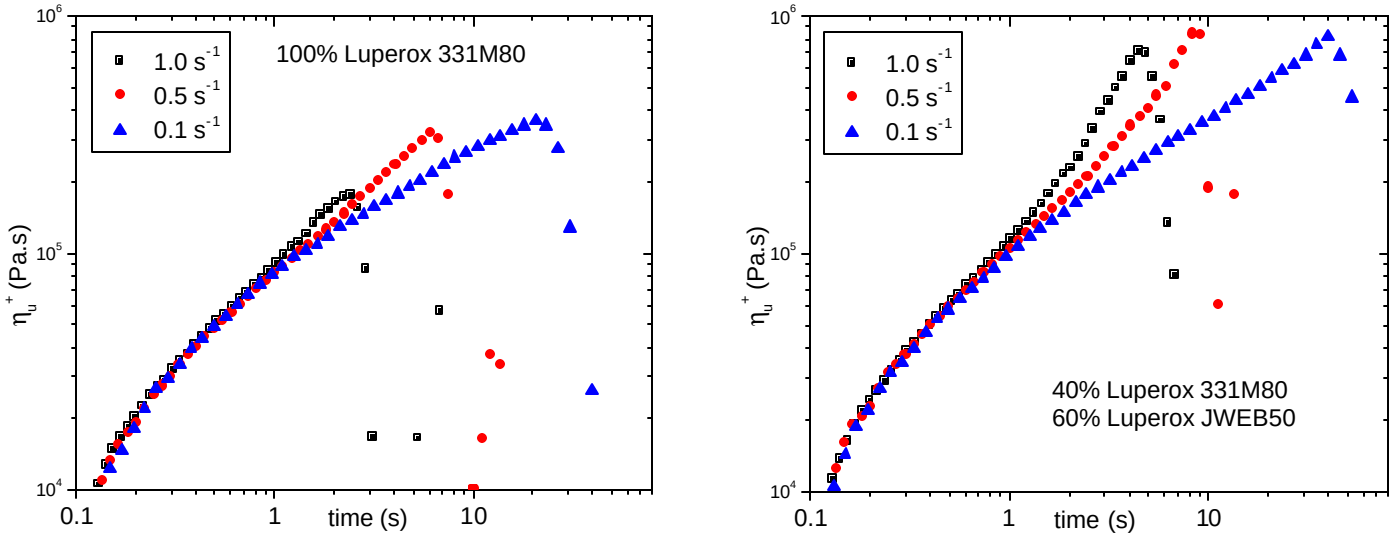
Conditions given in Table 2

Table 5. Shear rheology of PS prepared in continuous unit with Luperox® 331M80 and JWEB50; at equivalent A[O].

wt % JWEB50	MFI 5kg/200°C (dg/min)	h (Pa.s)	
		0.05 s-1	500 s-1
0	11.7	4,000	180
60	7.9	6,000	210

Conditions given in Table 2

Figure 1. Transient extensional viscosity measured using a Rheometrics RME at 160ºC



Luperox® JWEB50 Physical Characteristics

Peroxide Class	Assay (%)	Diluent	A[O] (wt%)	Appearance	Solubility	max. $T_{storage}$	SADT (by HAST)	Packaging
monoperoxy-carbonate	50	ethylbenzene	3.32 - 3.45	Colorless-to-pale-yellow liquid	insol. in H2O	38ºC 100ºF	70ºC	Fluorinated PE

Chemical name: Polyether poly(t-butyl peroxycarbonate)

Luperox® JWEB50 Decomposition Kinetics and Byproducts

Measured in ethylbenzene				Approximate in dodecane	Byproducts	
1 hr $T_{1/2}$ (ºC)	10 hr $T_{1/2}$ (ºC)	A (s^{-1})	Ea (kcal/mol)	1 hr $T_{1/2}$ (ºC)	Major	Trace
119	100	2.49×10^{15}	34.305	121	t-butanol, CO2, acetone, methane	polyether-polyols and polycarbonates

Luperox JWEB50 offers two advantages with respect to decomposition products:

- No acidic byproducts — Acid byproducts that can be produced from perketals and high half-life peresters can reduce reaction efficiency

- Lower extractable residuals — The multiple initiating sites on Luperox® JWEB50 increase the likelihood that initiator fragments will tie into the PS chain.

Luperox® JWEB50 is available in the Americas, Europe, and Asia

CAUTION: The chemical, physical, and toxicological properties of these R&D chemicals may not have been fully investigated. You must use due caution in handling of any such material and follow appropriate, good industrial hygiene and safety precautions to prevent human exposure. Carefully read and understand the information on the Material Safety Data Sheet (MSDS) before beginning work with the materials described in this brochure.

See MSDS for Health & Safety Considerations

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